Electronic Supporting Information (ESI) for:

Ring-opening polymerization of functionalized aliphatic bicyclic carbonates

Jixiang Ni,[a,b] *Matteo Lanzi,*[a]* *David H. Lamparelli,*[a] *Arjan W. Kleij*[a,c]*

[a] Institute of Chemical Research of Catalonia (ICIQ), The Barcelona Institute of Science and Technology (BIST), Av. Països Catalans 16, 43007 Tarragona, Spain

[b] Universitat Rovira i Virgili (URV), Marcel·lí Domingo s/n, 43007 Tarragona, Spain

[c] Catalan Institute of Research and Advanced Studies (ICREA), Pg. Lluís Companys 23, 08010 Barcelona, Spain

E-mail: mlanzi@iciq.es
E-mail: akleij@iciq.es

Contents

General remarks

Solvents were dried using an Innovative Technology PURE SOLV solvent purification system. Reactions were monitored by TLC and 1H NMR. TLC was carried out on 0.25 mm Merck aluminum-backed sheets coated with 60 F254 silica gel. Visualization of the silica plates was achieved using a UV lamp (λ = 254 nm) and/or by heating plates that were dipped in a ceric ammonium molybdate stain. Flash chromatography was carried out on Sigma Aldrich silica gel 60 (70-230 mesh) using the indicated eluent system. Benzyl alcohol (BnOH) was dried over calcium hydride and distilled under reduced pressure. TBD (1,5,7-triazabicyclo[4.4.0]dec-5-ene) was dissolved in DCM, stirred over calcium hydride, filtered and dried in vacuum prior to use.

NMR spectroscopy: NMR spectra were obtained on a Bruker 400 MHz, a 500 MHz or a 500 MHz with cryoprobe spectrometers equipped with probe-heads capable of producing gradients in the z direction with a maximum strength of 53.5 G/cm. ^{1}H, ^{13}C and ^{19}F NMR chemical shifts are reported in parts per million (ppm), relative to tetramethylsilane (TMS) for ^{1}H and ^{13}C with the residual solvent peak used as an internal reference. Multiplicities are reported as follows: singlet (s), broad band (br), d (doublet), dd (doublet of doublets), triplet (t) and multiplet (m).

Mass analysis: High resolution mass spectrometry (HRMS) data was recorded using two different methodologies depending on the complex to be analyzed. ESI-MS analyses were performed in a MicroTOF Focus mass spectrometer (Bruker Daltonics) by direct injection. Cold-spray ionization-MS (CSIMS) analyses were performed in a MicroTOF Focus mass spectrometer (Bruker Daltonics) equipped with a cold-spray ionization source by direct injection and using nitrogen as sprayer and dry gas.

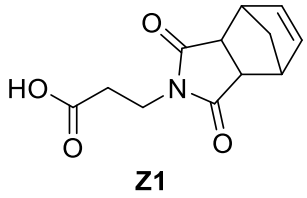
Thermal analysis: Differential scanning calorimetry (DSC) analyses for glass transition temperatures (T_g) determination were measured under an N_2 atmosphere using Mettler Toledo equipment (model DSC822e). Samples were weighed into 40 μL aluminum crucibles and subjected to three heating cycles at a heating rate of 10 °C/min. Thermogravimetric analyses (TGA) were recorded under an N_2 atmosphere using Mettler Toledo equipment (model TGA/SDTA851). Samples were weighed into 40 μL aluminum crucibles and heated to 600 ºC at a heating rate of 10 °C/min.

Gel permeation chromatography (GPC) measurements were performed using an Agilent 1200 series HPLC system, equipped with PSS SDV Analytical linear M GPC column (8 x 300 mm; 5 μm particle size) in tetrahydrofuran at 30 °C at a flow rate of 1 $mL \cdot min^{-1}$. Samples were analyzed at a concentration of 1 $mg \cdot mL^{-1}$ after filtration through a 0.45 μm pore-size membrane. M_n, M_w, and $Đ$ data were derived from the RI signal by a calibration curve based on polystyrene standards (PS from Polymer Standards Service) for the analysis of the polymers. The GPC samples were prepared by dissolving

the polymer (3−5 mg) in THF (2 mL) and filtering the solution through a 0.45 μm pore-size membrane.

Ligand **L1**, and catalysts **C1** and **C2** were prepared according to previously reported procedures.[1,2,3] All the monomers were dissolved in dichloromethane (1 to 5 mL) and allowed to stir for 16 h with CaH_2 before the AROP experiments. The solid was removed through filtration, the residue solvent was evaporated under vacuum yielding the corresponding dry monomer, which was used without further purification.

Synthesis of precursor Z1:

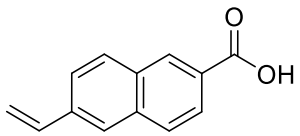


Z1

3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisoindol-2-yl)propanoic acid Z1: An oven-dried flask was charged with 3a,4,7,7a-tetrahydro-4,7-methanoisobenzofuran-1,3-dione (2.5 g, 15.2 mmol, 1 equiv) and 3-aminopropanoic acid (1.7 g, 19 mmol, 1.25 equiv). The flask was evacuated and back-filled with nitrogen three times. Then, triethyl amine (270 μL, 0.125 mmol, 13 mol%) and toluene (10 mL, 1.52 M) were added. The resulting mixture was allowed to stir at reflux temperature for 16 h under a nitrogen atmosphere. The crude mixture was allowed to cool to room temperature, and concentrated under vacuum. The residue was dissolved in CH_2Cl_2, the organic phase was washed with 1 N HCl and NaCl, dried over Na_2SO_4 and concentrated to afford **Z1** in 50% yield as white solid (1.8 g, 7.65 mmol). The spectral data of **Z1** correspond to the literature.[4]

^{1}H NMR (300 MHz, $CDCl_3$) δ 6.08 (t, *J* = 1.9 Hz, 2H), 3.65 (t, *J* = 7.4 Hz, 2H), 3.39 (dh, *J* = 3.4, 1.7 Hz, 2H), 3.26 (dd, *J* = 3.0, 1.5 Hz, 2H), 2.54 (dd, *J* = 7.8, 7.0 Hz, 2H), 1.73 (dt, *J* = 8.8, 1.7 Hz, 1H), 1.53 (dt, *J* = 8.8, 1.5 Hz, 1H).

Synthesis of precursor Z2:

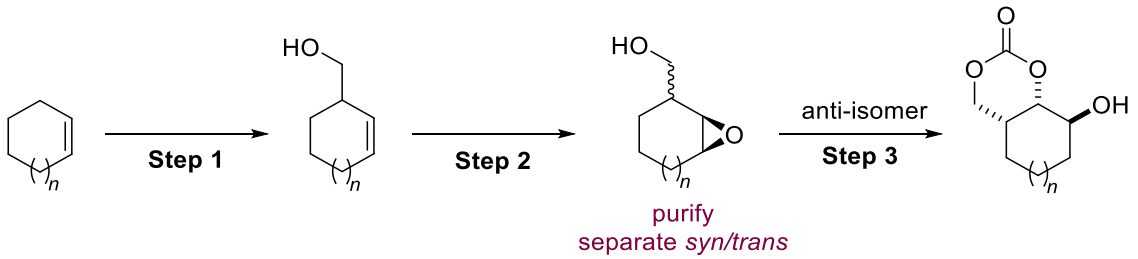


Z2

6-vinyl-2-naphthoic acid Z2: A Schlenk tube equipped with a magnetic stirrer was charged with potassium vinyltrifluoroborate (500 mg, 3.73 mmol, 1 equiv), $PdCl_2$ (13 mg, 0.075 mmol, 2 mol%), PPh_3 (60 mg, 0.23 mmol, 6 mol%), Cs_2CO_3 (3.68 g, 11.3 mmol, 3 equiv) and methyl 6-bromo-2-naphthoate (1 g, 3.77 mmol, 1 equiv). The tube was evacuated and backfilled with argon three times, and then 7 mL of THF and 0.75 mL of H_2O were added. The reaction mixture was stirred at 85 °C for 16 h. The reaction mixture was allowed to cool to room temperature, then diluted with H_2O followed by extraction with DCM, dried with anhydrous Na_2SO_4 and concentrated in vacuo. The product was obtained in quantitative yield and it was used without further purification for the next step. To a solution of the crude product in THF (13 mL) was added H_2O (13 mL) followed by LiOH monohydrate (525 mg, 19 mmol, 5 equiv). The resulting mixture was stirred for 5 h at room temperature. The reaction mixture was concentrated under a vacuum, and then 1 M HCl was added till pH 5. The white precipitate that formed was collected, washed with Et_2O and dried under a high vacuum to give **Z2** in 57% overall yield (430 mg, 2.16 mmol).

^{1}H NMR (400 MHz, DMSO) δ 8.54 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 1H), 7.99 (dd, *J* = 8.5, 1.6 Hz, 1H), 7.96 – 7.93 (m, 2H), 7.81 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.94 (dd, *J* = 17.6, 11.0 Hz, 1H), 6.05 (dd, *J* = 17.6, 0.9 Hz, 1H), 5.43 (dd, *J* = 10.8, 0.8 Hz, 1H). **^{13}C NMR** (101 MHz, DMSO) δ 167.7, 136.5 (2C), 134.9, 131.9, 129.8, 129.5, 127.9 (2C), 126.0, 125.8, 123.8, 115.9. **HRMS** (ESI): m/z $[M-H]^-$ calcd for $C_{13}H_9O_2$: 197.0608; found: 196.0612. **IR** (neat) ν_{max} = 3389, 1679 (C=O), 1624 cm^{-1}.

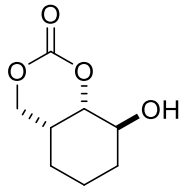
General procedure for the preparation of bicyclic precursors A-D



Step 1 (example): A 500 mL round bottom flash was charged with cyclohexene (54 mL, 0.53 mol) and KO*t*Bu (6.8 g, 60.4 mmol), and the resulting suspension was degassed for 30 min with argon. The resulting mixture was cooled to 0°C and *n*BuLi (1.6 M in hexanes, 40 mL, 64 mmol) was added dropwise, and the mixture then stirred at the same temperature for 2 h. Then it was allowed to warm to room temperature and stirred for a further 16 h. The resultant pale-yellow suspension was cooled to 0 °C and $(HCHO)_n$ (2 g, 66.4 mmol) was added. The reaction mixture was allowed to warm to room temperature and heated to 60 ºC for 3 h. Subsequently, the mixture was cooled to 0 °C and quenched with a saturated aqueous $NaHCO_3$ solution (40 mL). The mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic phases were washed sequentially with a saturated aqueous $NaHCO_3$ solution (40 mL) and brine (40 mL), dried over $MgSO_2$, concentrated in vacuo to give the desired product in 76% (5.1 g, 44.6 mmol) as colorless oil.

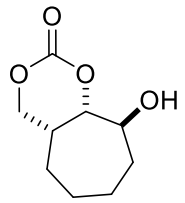
Step 2: To a solution of the product of step 1 (2.5 g, 22.3 mmol, 1 equiv.) in dry MeOH (112 mL, 0.2 M) at 0 °C, *m*CPBA (7.5 g, 33.5 mmol, 1.5 equiv, 77%) was added portion-wise. The reaction was allowed to warm to room temperature and stirred for 16 h. The solvent was removed, the residue was dissolved in DCM and then washed with Na_2CO_3. The organic phase was dried over $MgSO_4$, concentrated and purified through column chromatography (hexane:ethyl acetate, 6:4 v/v) to obtain the target homoallylic alcohol product as a colorless oil in 84% as a 1:1 mixture of *syn* and *anti*-isomers (2.39 g, 18.6 mmol).

Step 3: A 25 mL stainless-steel reactor was charged the product of step 2 (1.2 g, 9.3 mmol, 1 equiv), MEK (5 mL, 1.86 M), **C1** (100 mg, 0.19 mmol, 2 mol%) and DIPEA (175 μL, 0.94 mmol, 10 mol%). The reactor was purged three times and then then charged with CO_2 (10 bar). The mixture was stirred at 100 °C for 22 h, then cooled with an ice/water bath and carefully depressurized. The solvent was removed in vacuo and the resulting product was purified by flash chromatography (hexane:ethyl acetate, 1:1 v/va) affording the desired product in 85% as a pale-yellow solid (735 mg, 4.27 mmol).



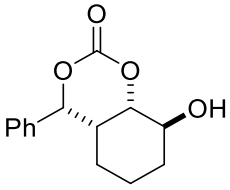
A

8-hydroxyhexahydro-4*H*-benzo[d][1,3]dioxin-2-one A: ^{1}H NMR (300 MHz, $CDCl_3$) δ 4.46 – 4.40 (m, 2H), 4.26 (dd, *J* = 11.1, 3.9 Hz, 1H), 4.07 – 4.03 (m, 1H), 2.44 – 2.31 (m, 2H), 1.85 – 1.70 (m, 2H), 1.67 – 1.52 (m, 4H). The spectral data correspond to the literature.[5]



B

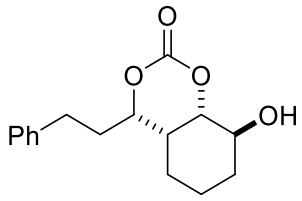
9-hydroxyoctahydrocyclohepta[*d*][1,3]dioxin-2-one B: Following the overall procedure (steps 1-3) using cycloheptene (7 mL, 60 mmol, 1 equiv, in 50 mL cyclohexane) **B** was obtained in 13% (248 mg, 1.13 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 4.61 – 4.58 (m, 1H), 4.44 (dd, *J* = 11.0, 3.6 Hz, 1H), 4.16 (dd, *J* = 11.0, 3.6 Hz, 1H), 3.93 – 3.88 (m, 1H), 2.65 (brs, 1H), 2.31 – 2.24 (m, 1H), 2.01 – 1.89 (m, 3H), 1.72 – 1.61 (m, 3H), 1.65 – 1.45 (m, 1H), 1.43 – 1.35 (m, 1H). The spectral data correspond to the literature.[5]



C

8-hydroxy-4-phenylhexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one C: A modified procedure (regarding step 1) was followed: To a 10 mL Schlenk flask was sequentially added iron powder (1.7 g, 30 mmol, 1.9 equiv) and DMSO (20 mL). Then the iron was activated by the addition of 1,2-dibromoethane (280 μL, 3.2 mmol, 0.2 equiv) and TMSCl (406 μL, 3.2 mmol, 0.2 equiv). After stirring for 30 min, $BiCl_3$ (1 g, 3.2 mmol, 0.2 equiv), 3-bromocyclohexene (2.8 mL, 24 mmol, 1.5 equiv) and freshly distilled benzaldehyde (1.6 mL, 16 mmol, 1 equiv) were sequentially added to the reaction mixture. The suspension was vigorously stirred at r.t. for 24 h before quenching it with a saturated aqueous $NaHCO_3$ solution (60 mL) following extraction by ethyl acetate (3 × 20 mL).

The combined extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue obtained was purified by silica gel column chromatography to give the pure product. Subsequently the product was used in steps 2+3. Following this procedure, the target product was obtained in 32% as a colorless oil (434 mg, 1.75 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.41 – 7.37 (m, 2H), 7.35 – 7.29 (m, 3H), 5.63 (d, *J* = 3.1 Hz, 1H), 4.71 (t, *J* = 3.1 Hz, 1H), 4.18 (q, *J* = 3.0 Hz, 1H), 2.47 (ddt, *J* = 12.8, 5.5, 2.9 Hz, 1H), 1.81 – 1.68 (m, 2H), 1.62 – 1.48 (m, 2H), 1.26 – 1.10 (m, 2H). The spectral data correspond to the literature.[5]

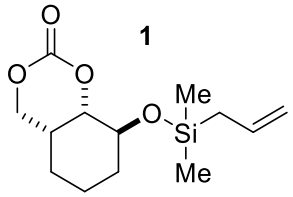


D

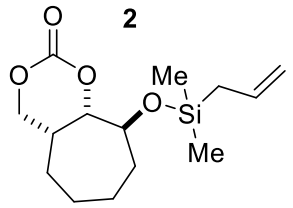
8-hydroxy-4-phenethylhexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one D: A modified procedure (regarding step 1) was used: To a 10 mL Schlenk flask was sequentially added iron powder (1.7 g, 30 mmol, 1.9 equiv.) and DMSO (20 mL). Then the iron was activated by the addition of 1,2-dibromoethane (280 μL, 3.2 mmol, 0.2 equiv) and TMSCl (406 μL, 3.2 mmol, 0.2 equiv). After stirring for 30 min, $BiCl_3$ (1 g, 3.2 mmol, 0.2 equiv), 3-bromocyclohexene (2.8 mL, 24 mmol, 1.5 equiv) and freshly distilled 3-phenylpropionaldehyde (2 mL, 16 mmol, 1 equiv) were sequentially added to the reaction mixture. The suspension was vigorously stirred at r.t. for 24 h before quenching it with a saturated aqueous $NaHCO_3$ solution (60 mL) following extraction with ethyl acetate (3 × 20 mL). The combined extracts were washed with brine (30 mL), dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue obtained was purified by silica gel column chromatography to give the pure product. Subsequently the product was used for steps 2+3. Following this sequence of events, the target product was obtained in 60% as a colorless oil (441 mg, 1.60 mmol). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.35 – 7.31 (m, 2H), 7.26 – 7.21 (m, 3H), 4.44 – 4.41 (m, 2H), 4.12 – 4.10 (m, 1H), 2.88 (ddd, *J* = 14.3, 9.2, 5.3 Hz, 1H), 2.73 (ddd, *J* = 13.9, 8.9, 7.3 Hz, 1H), 2.21 – 2.15 (m, 1H), 2.14 – 2.07 (m, 1H), 1.88 – 1.80 (m, 1H), 1.76 – 1.64 (m, 4H), 1.41 – 1.29 (m, 2H). The spectral data correspond to the literature.[5]

General procedure for the preparation of silyl ethers derivatives

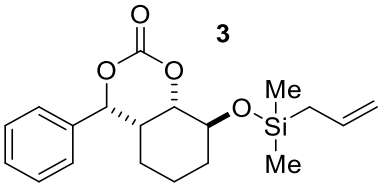
To a solution of one of the precursors **A-D** (1 equiv) and triethyl amine (5 equiv) in dry DCM (0.1 M), the respective chlorosilane (3 equiv) was added dropwise. The resulting mixture was stirred at room temperature for 3 h. The solvent was removed and the crude was purified by column chromatography (hexane/ethyl acetate) to give the desired product.



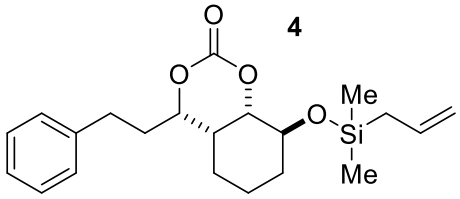
8-((allyldimethylsilyl)oxy)hexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one (1): Following the general procedure using **A** (390 mg, 2.26 mmol) and allyl(chloro)dimethylsilane, monomer **1** was obtained in 66% yield (405 mg, 1.50 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.81 – 5.70 (m, 1H), 4.92 – 4.86 (m, 2H), 4.45 (ddd, *J* = 11.0, 3.7, 1.2 Hz, 1H), 4.33 (t, *J* = 3.5 Hz, 1H), 4.17 (dt, *J* = 11.0, 1.7 Hz, 1H), 4.01 (d, *J* = 3.1 Hz, 1H), 2.24 (dt, *J* = 13.6, 4.8 Hz, 1H), 1.76 – 1.50 (m, 8H), 0.13 (s, 6H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.1, 133.5, 114.1, 78.9, 72.9, 67.1, 27.6, 27.3, 24.6, 22.6, 17.7, -2.1, -2.1. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{22}NaO_4Si$: 293.1180; found: 293.1183. **IR** (neat) ν_{max} = 2940, 2869, 1751 (C=O) cm^{-1}.



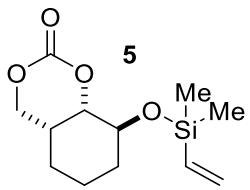
9-((allyldimethylsilyl)oxy)octahydrocyclohepta[*d*][1,3]dioxin-2-one (2): Following the general procedure using **B** (390 mg, 2.09 mmol) and allyl(chloro)dimethylsilane, **2** was obtained in 55% yield (326 mg, 1.15 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.82 (ddt, *J* = 17.0, 10.1, 8.1 Hz, 1H), 4.95 – 4.88 (m, 2H), 4.55 (ddd, *J* = 5.5, 4.2, 1.2 Hz, 1H), 4.45 (dd, *J* = 10.9, 3.2 Hz, 1H), 4.18 (dd, *J* = 10.8, 2.2 Hz, 1H), 3.92 (ddd, *J* = 9.3, 5.7, 1.9 Hz, 1H), 2.18 – 2.13 (m, 1H), 1.94 – 1.85 (m, 2H), 1.81 – 1.61 (m, 6H), 1.51 – 1.43 (m, 2H), 0.19 (s, 3H), 0.19 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.7, 133.8, 113.9, 87.0, 75.5, 73.8, 34.3, 31.7, 27.9, 26.3, 24.8, 24.5, -1.9, -2.0. **HRMS** (ESI): m/z $[M-C_5H_{11}Si+Na]^+$ calcd for $C_9H_{14}NaO_4$: 209.0784; found: 209.0780. **IR** (neat) ν_{max} = 3411, 2928, 2860, 1720 (C=O), 1109 cm^{-1}.



8-((allyldimethylsilyl)oxy)-4-phenylhexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one (3): Following the general procedure using **C** (433 mg, 1.74 mmol) and allyl(chloro)dimethylsilane, **3** was obtained in 78% yield (468 mg, 1.35 mmol) as a colorless oil. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.31 (m, 3H), 5.79 (ddt, *J* = 16.9, 10.1, 8.0 Hz, 1H), 5.61 (d, *J* = 3.1 Hz, 1H), 4.96 – 4.89 (m, 2H), 4.52 (t, *J* = 3.1 Hz, 1H), 4.10 (q, *J* = 2.9 Hz, 1H), 2.41 (ddt, *J* = 12.8, 5.3, 2.9 Hz, 1H), 1.68 – 1.53 (m, 5H), 1.45 – 1.40 (m, 1H), 1.23 – 1.10 (m, 2H), 0.16 (s, 3H), 0.16 (s, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 148.4, 136.0, 133.5, 128.5, 128.2, 125.1, 114.1, 82.9, 79.6, 67.2, 33.2, 27.3, 24.7, 18.1, 17.4, -2.0, -2.1. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{26}NaO_4Si$: 369.1493; found: 369.1495. **IR** (neat) ν_{max} = 2944, 2869, 1748 (C=O) cm^{-1}.

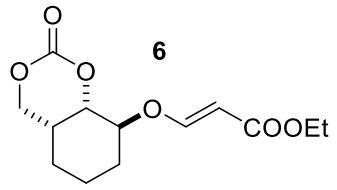


8-((allyldimethylsilyl)oxy)-4-phenethylhexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one (4): Following the general procedure using **D** (441 mg, 1.59 mmol) and allyl(chloro)dimethylsilane, **4** was obtained in 73% yield (433 mg, 1.15 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.33 – 7.29 (m, 2H), 7.24 – 7.19 (m, 3H), 5.75 (ddt, *J* = 17.0, 10.1, 8.1 Hz, 1H),4.91 – 4.85 (m, 2H), 4.37 (ddd, *J* = 9.3, 4.3, 2.8 Hz, 1H), 4.24 (t, *J* = 3.1 Hz, 1H), 4.02 (brs, 1H), 2.88 (ddd, *J* = 14.2, 9.2, 5.3 Hz, 1H), 2.72 (ddd, *J* = 13.9, 8.9, 7.4 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.84 – 1.76 (m, 1H), 1.69 – 1.65 (m, 2H), 1.63 – 1.52 (m, 5H), 1.33 – 1.25 (m, 1H), 0.12 (s, 3H), 0.12 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.7, 140.5, 133.5, 128.6, 128.5, 126.3, 114.1, 81.6, 79.6, 67.0, 33.2, 31.1, 30.8, 27.3, 24.7, 18.0, 17.3, -2.0, -2.1. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{21}H_{30}NaO_4Si$: 397.1806; found: 397.1810. **IR** (neat) ν_{max} = 2944, 1749 (C=O) cm^{-1}.



8-((dimethyl(vinyl)silyl)oxy)hexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one (5): Following the general procedure using **A** (386 mg, 2.24 mmol) and chloro(dimethyl)vinylsilanes, **5** was obtained in 88% yield (503 mg, 1.96 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.14 – 6.01 (m, 2H), 5.79 (dd, *J* = 19.7, 4.4 Hz, 1H), 4.45 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.18 (dd, *J* = 11.0, 1.8 Hz, 1H), 4.01 (q, *J* = 3.2 Hz, 1H), 2.28 – 2.23 (m, 1H), 1.79 – 1.70 (m, 1H), 1.68 – 1.49 (m, 6H), 0.19 (d, *J* = 0.8 Hz, 6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 148.1, 136.9, 133.8, 78.9, 72.8, 67.1, 27.6, 27.2, 22.6, 17.8, -1.8, -1.9. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{12}H_{20}NaO_4Si$: 279.1023; found: 279.1033. **IR** (neat) ν_{max} = 2939, 2884, 1749 cm^{-1}.

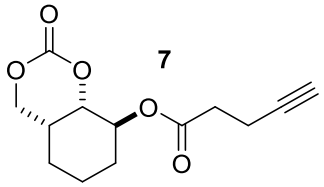
Synthesis of monomer 6



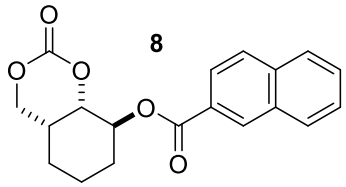
Ethyl (*E*)-3-((2-oxohexahydro-4*H*-benzo[*d*][1,3]dioxin-8-yl)oxy)acrylate (6): To a stirred solution of **A** (386 mg, 2.24 mmol, 1 equiv) in CH_3CN (11 mL, 0.2 M), N-methyl-morpholine (NMM, 50 μL, 0.45 mmol, 0.2 equiv) was added followed by ethyl propiolate (275 μL, 2.65 mmol, 1.2 equiv). The resulting mixture was allowed to stir at room temperature for 16 h. The solvent was removed and the crude was purified by column chromatography to give the etherified product **6** in 56% yield (344 mg) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.46 (d, *J* = 12.5 Hz, 1H), 5.31 (d, *J* = 12.5 Hz, 1H), 4.60 (t, *J* = 3.3 Hz, 1H), 4.49 (dd, *J* = 11.1, 3.6 Hz, 1H), 4.27 (q, *J* = 3.2 Hz, 1H), 4.21 (dd, *J* = 11.2, 1.7 Hz, 1H), 4.15 (q, *J* = 7.2 Hz, 2H), 2.23 – 2.20 (m, 1H), 1.91 – 1.87 (m, 1H), 1.79 – 1.72 (m, 1H), 1.68 – 1.56 (m, 4H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.2, 159.9, 147.3, 99.2, 76.1, 75.6, 72.4, 60.0, 28.0, 24.1, 22.1, 17.8, 14.3. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{13}H_{18}NaO_6$: 293.0996; found: 293.1006. **IR** (neat) ν_{max} = 2940, 2870, 1749, 1701, 1639, 1621 cm^{-1}.

General procedure for the preparation of ester-derivatives

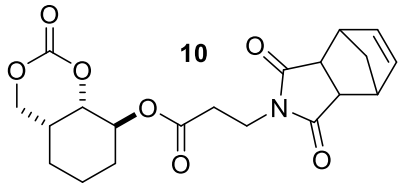
To a solution of **A** (1 equiv) and DMAP (0.1 equiv) in dry DCM (0.2 M) the desired carboxylic acid was added (1.05 equiv) followed by the *N*,*N'*-dicyclohexylcarbodiimide (DCC, 1.1 equiv; 1 M in DCM). The resulting mixture was stirred at room temperature for 2 h. The white precipitate was filtered off, the resulting organic phase was washed twice with sutured solution of Na_2CO_3, dried over $MgSO_4$, filtered and concentrated under vacuum. The crude was purified by column chromatography (hexane/ethyl acetate) to give the desired product.



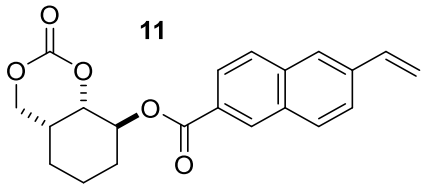
2-oxohexahydro-4*H*-benzo[*d*][1,3]dioxin-8-yl pent-4-ynoate (7): Following the general procedure using **A** (730 mg, 4.24 mmol) and 4-pentynoic acid, **7** was obtained in 67% (712 mg, 2.86 mmol) as a pale-yellow oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.15 (q, *J* = 3.9 Hz, 1H), 4.55 (t, *J* = 3.7 Hz, 1H), 4.46 (dd, *J* = 11.1, 3.8 Hz, 1H), 4.24 (dd, *J* = 11.1, 2.5 Hz, 1H), 2.60 – 2.57 (m, 2H), 2.54 – 2.51 (m, 2H), 2.26 – 2.23 (m, 1H), 1.98 (t, *J* = 2.6 Hz, 1H), 1.84 – 1.75 (m, 2H), 1.70 – 1.62 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.3, 147.5, 82.1, 76.0, 72.0, 69.3, 68.9, 33.4, 28.6, 24.6, 22.4, 18.5, 14.5. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for: $C_{13}H_{16}NaO_5$: 275.0890; found: 275.0898. **IR** (neat) ν_{max} = 3279, 2938, 1736 (C=O) cm^{-1}.



2-oxohexahydro-4*H*-benzo[*d*][1,3]dioxin-8-yl 2-naphthoate (8): Following the general procedure using **A** (390 mg, 2.26 mmol) and 2-naphthoic acid, **8** was obtained in 72% (531 mg, 1.63 mmol) as a white solid. Column chromatography conditions: hexane/ethyl acetate 8:2 v/v). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (s, 1H), 8.05 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.99 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.92 (d, *J* = 8.3 Hz, 2H), 7.64 (ddd, *J* = 8.2, 6.8, 1.4 Hz, 1H), 7.59 (ddd, *J* = 8.1, 6.8, 1.3 Hz, 1H), 5.44 (q, *J* = 3.5 Hz, 1H), 4.78 (t, *J* = 3.6 Hz, 1H), 4.54 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.30 (dd, *J* = 11.1, 2.3 Hz, 1H), 2.41 – 2.37 (m, 1H), 2.00 – 1.97 (m, 2H), 1.92 – 1.84 (m, 1H), 1.83 – 1.72 (m, 2H), 0.92 – 0.86 (m, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 147.5, 135.7, 132.4, 131.2, 129.3, 128.6, 128.4, 127.8, 126.9, 126.8, 125.0, 76.0, 72.1, 69.1, 28.8, 24.6, 22.5, 18.8. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{19}H_{18}NaO_5$: 349.1046; found: 349.1045. **IR** (neat) ν_{max} = 2938, 2868, 1750 (*C*=*O*OR), 1711 (C=O) cm^{-1}.

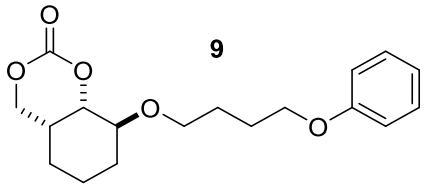


2-oxohexahydro-4*H*-benzo[*d*][1,3]dioxin-8-yl 3-(1,3-dioxo-1,3,3a,4,7,7a-hexahydro-2*H*-4,7-methanoisoindol-2-yl)propanoate (10): Following the general procedure using **A** (420 mg, 2.43 mmol) and **Z1** (603 mg, 2.56 mmol, 1.05 equiv), **10** was obtained in 66% (620 mg, 1.59 mmol) as a white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.08 (s, 1H), 5.07 (q, *J* = 3.6 Hz, 1H), 4.54 (t, *J* = 3.6 Hz, 1H), 4.51 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.23 (dd, *J* = 11.1, 2.4 Hz, 1H), 3.70 – 3.59 (m, 2H), 3.39 – 3.37 (m, 2H), 3.26 – 3.26 (m, 2H), 2.50 (t, *J* = 7.1 Hz, 2H), 2.26 – 2.23 (m, 1H), 1.18 – 1.53 (m, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.3, 177.3, 169.2, 147.6, 134.5, 134.4, 75.7, 72.1, 68.9, 52.2, 45.8, 45.7, 44.9, 44.9, 34.0, 32.6, 28.5, 24.4, 22.3, 18.5. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{20}H_{23}NNaO_7$: 412.1367; found: 412.1383. **IR** (neat) ν_{max} = 2945, 2870, 1741 (C=O), 1692 (C=O) cm^{-1}.



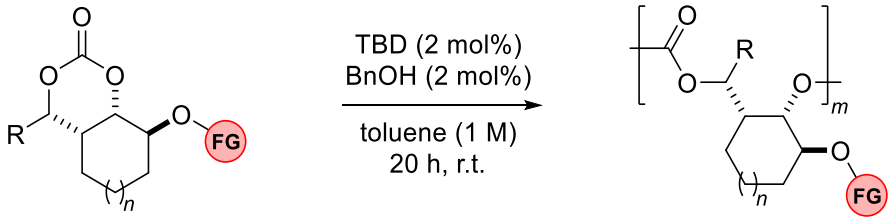
2-oxohexahydro-4*H*-benzo[*d*][1,3]dioxin-8-yl 6-vinyl-2-naphthoate (11): Following the general procedure using **A** (340 mg, 1.97 mmol) and **Z2** (430 mg, 2.17 mmol, 1.1 equiv) **11** was obtained in 54% (376 mg, 1.07 mmol) as white solid. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.01 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.91 (d, *J* = 8.6 Hz, 1H), 7.85 (d, *J* = 8.6 Hz, 1H), 7.79 (s, 1H), 7.71 (dd, *J* = 8.6, 1.7 Hz, 1H), 6.89 (dd, *J* = 17.6, 10.9 Hz, 1H), 5.94 (d, *J* = 17.6 Hz, 1H), 5.44 – 5.40 (m, 2H), 4.75 (t, *J* = 3.6 Hz, 1H), 4.51 (dd, *J* = 11.1, 3.7 Hz, 1H), 4.28 (dd, *J* = 11.1, 2.3 Hz, 1H), 2.38 – 2.35 (m, 1H), 1.97 – 1.95 (m, 2H), 1.87 – 1.73 (m, 4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 147.5, 137.7, 136.4, 135.9, 132.0, 130.9, 129.5, 128.4, 126.7, 126.0, 125.5, 124.3, 115.9, 76.0, 72.1, 69.1, 28.7, 24.6, 22.4, 18.8. **HRMS** (ESI): m/z $[M+H]^+$ calcd for $C_{21}H_{21}O_5$: 353.1384; found: 353.1381. **IR** (neat) ν_{max} = 2936, 1765 (C=O), 1712 (C=O) cm^{-1}.

Synthesis of monomer 9

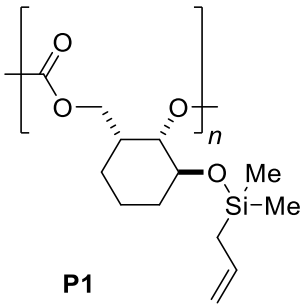


8-(4-phenoxybutoxy)hexahydro-4*H*-benzo[*d*][1,3]dioxin-2-one (9): To a stirred solution of **A** (277 mg, 1.61 mmol, 1 equiv.) in dry THF (9.5 mL, 0.17 M), was added 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (470 μL, 1.93 mmol, 1.2 equiv) followed by 18-crown-6 (510 mg, 1.93 mmol, 1.2 equiv) and dry KF (112 mg, 1.93 mmol, 1.2 equiv). The resulting mixture was allowed to stir at room temperature for 120 h. The solvent was removed and the crude was purified by column chromatography giving **9** in 49% yield (255 mg, 0.79 mmol) as a colorless oil. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (m, 2H), 6.94 (tt, *J* = 7.4, 1.1 Hz, 1H), 6.90 – 6.88 (m, 2H), 4.50 (t, *J* = 3.3 Hz, 1H), 4.43 (dd, *J* = 11.0, 3.7 Hz, 1H), 4.16 (dd, *J* = 11.0, 1.7 Hz, 1H), 3.99 (t, *J* = 6.3 Hz, 2H), 3.65 – 3.59 (m, 2H), 3.49 (dt, *J* = 9.2, 6.1 Hz, 1H), 2.18 – 2.15 (m, 1H), 1.89 – 1.72 (m, 5H), 1.6 7 -1.53 (m, 5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.9, 148.2, 129.4, 120.6, 114.4, 77.2, 73.8, 72.7, 68.9, 67.4, 28.2, 26.6, 26.2, 23.6, 22.5, 18.1. **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{24}NaO_5$: 343.1516; found: 343.1515. **IR** (neat) ν_{max} = 2937, 2867, 1748 (C=O) cm^{-1}.

General procedure for the ring-opening polymerization

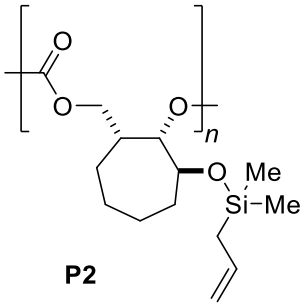


In a nitrogen-filled glovebox, a vial equipped with a stirring bar was charged with the desired monomer (1 equiv) followed by benzyl alcohol (59.2 mM stock solution in toluene, 2.0 mol%) and TBD (29.5 mM stock solution in toluene, 2 mol%). The resulting homogeneous solution was stirred for 20 h at room temperature. Then, the reaction mixture was quenched with benzoic acid (stock solution in toluene, 12 µmol, 83 mM) and a sample was analyzed by ^{1}H NMR ($CDCl_3$) to determine the conversion. Precipitation from DCM/MeOH provided the purified polymer product as a white solid, which was collected by filtration and dried in a vacuum drying oven at 40 °C for three days.



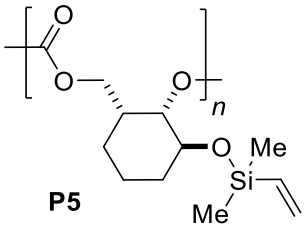
P1

P1 was obtained following the general procedure using monomer **1** (159 mg, 0.59 mmol). The conversion of **1** was determined by ^{1}H NMR to be 91%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.78 – 5.74 (1H), 4.91 – 4.85 (2H), 4.62 (1H), 4.11 – 3.97 (3H), 2.37 (1H), 1.65 (1H), 1.62 – 1.40 (7H), 0.13 – 0.13 (6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2, 154.7, 154.1, 133.9, 133.7, 114.0, 113.8, 75.9, 75.5, 68.6, 66.7, 36.6, 34.6, 28.7, 24.9, 24.9, 24.7, 24.7, 24.7, 23.2, 22.5, 22.1, 19.2, 19.0, 18.8, 18.5, -1.7, -1.8, -1.9, -2.0, -2.1, -2.1, -2.1, -2.2, -2.2. **IR** (neat) ν_{max} = 2939, 2867, 1742, 1238 cm^{-1}. **DSC**: T_g (º C) = 19. **TGA**: T_d^5 (ºC) = 282. **GPC**: M_n = 5.56 kg/mol, M_w = 8.59 kg/mol, $Đ$ = 1.55.



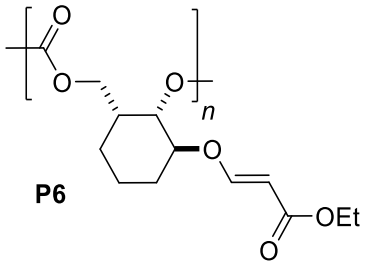
P2

P2 was obtained following the general procedure using monomer **2** (82 mg, 0.29 mmol). Conversion of **2** was determined by ^{1}H NMR at 86%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.82 – 5.71 (1H), 4.90 – 4.86 (2H), 4.84 – 4.656 (1H), 4.03 – 3.96 (3H), 2.37 – 2.04 (1H), 1.83 – 1.25 (10), 0.15 – 0.11 (6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2, 154.8, 154.4, 133.9, 133.9, 113.8, 113.7, 83.2, 79.8, 79.3, 73.6, 73.2, 70.0, 69.5, 40.6, 40.0, 36.0, 32.6, 32.0, 31.8, 29.7, 29.2, 28.9, 27.5, 25.9, 24.9, 24.7, 24.7, 23.6, 23.2, 22.5, 19.8, -1.9, -1.9, -2.0, -2.0, -2.0, -2.1, -2.1, -2.2, -2.2, -2.2. **IR** (neat) ν_{max} = 2931, 2865, 1742, 1243 cm^{-1}. **DSC**: T_g (º C) = 11. **TGA**: T_d^5 (º C) = 307. **GPC**: M_n = 6.82 kg/mol, M_w = 1.12 kg/mol, $Đ$ = 1.64.



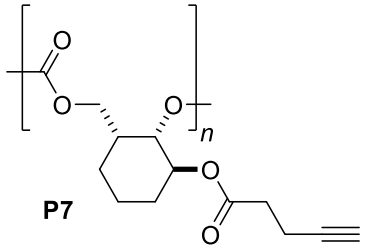
P5

P5 was obtained following the general procedure using monomer **5** (148 mg, 0.58 mmol). Conversion of **5** was determined by ^{1}H NMR at 95%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.16 – 6.09 (1H), 6.02 – 5.98 (1H), 5.80 – 5.76 (1H), 4.64 – 6.62 (1H), 4.09 – 3.91 (3H), 2.38 - 2.07 (1H), 1.69 – 1.40 (6H), 0.19 (6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 155.2, 154.7, 154.6, 154.1, 137.5, 137.5, 137.4, 137.1, 133.5, 133.5, 133.5, 133.2, 133.2, 133.2, 75.6, 75.4, 75.3, 75.2, 68.9, 68.6, 68.4, 66.8, 36.6, 34.6, 34.5, 28.6, 25.0, 23.2, 22.1, 19.3, 19.2, 19.1, 18.5, 1.0, -1.5, -1.5, -1.6, -1.7, -1.8, -1.8, -1.9. **IR** (neat) ν_{max} = 2944, 1745, 1252 cm^{-1}. **DSC**: T_g (º C) = 57; **TGA**: T_d^5 (º C) = 277. **GPC**: M_n = 1.17 kg/mol, M_w = 1.69 kg/mol, $Đ$ = 1.44.



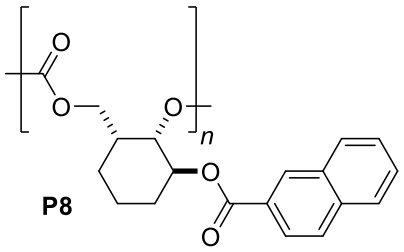
P6

P6 was obtained following the general procedure using monomer **6** (78 mg, 0.29 mmol). Conversion of **6** was determined by ^{1}H NMR at 89%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.51 – 7.47 (1H), 5.41 – 5.33 (1H), 4.85 (1H), 4.30 – 3.93 (5H), 2.30 (1H), 1.83 – 1.44 (6H), 1.27 – 1.25 (3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 167.6, 160.6, 155.1, 155.0, 154.4, 154.3, 153.8, 98.6, 75.6, 67.8, 59.9, 59.8, 40.8, 35.2, 28.7, 25.6, 25.2, 22.6, 22.3, 18.6, 14.4, 14.3, 14.2. **IR** (neat) ν_{max} = 2940, 1745, 1710, 1251, 1130 cm^{-1}. **DSC**: T_g (º C) = 70; **TGA**: T_d^5 (º C) = 268. **GPC**: M_n = 5.00 kg/mol, M_w = 6.84 kg/mol, $Đ$ = 1.36.



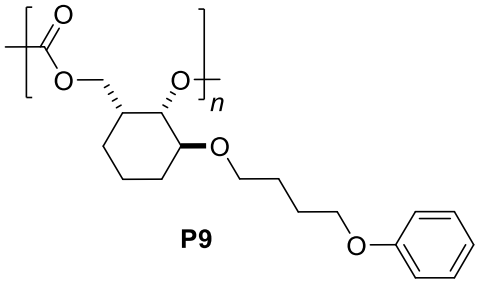
P7

P7 was obtained following the general procedure using monomer **7** (75 mg, 0.30 mmol). Conversion of **7** was determined by ^{1}H NMR at 98%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 5.10 – 5.06 (1H), 4.85 – 4.79 (1H), 4.15 – 3.95 (2H), 2.58 – 2.51 (4H), 2.36 – 2.30 (1H), 2.04 – 2.01 (1H), 1.81 – 1.76 (2H), 1.60 – 1.55 (4H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 170.4, 154.2, 128.6, 128.3, 82.3, 72.4, 69.4, 68.8, 68.6, 67.8, 35.7, 33.6, 33.5, 31.6, 29.0, 25.6, 22.6, 21.0, 18.9, 14.5, 14.4, 14.2, 14.1, 11.4. **IR** (neat) ν_{max} = 3296, 2943, 1736, 1233 cm^{-1}. **DSC**: T_g (º C) = 41; **TGA**: T_d^5 (º C) = 246. **GPC**: M_n = 6.86 kg/mol, M_w = 8.88 kg/mol, $Đ$ = 1.29.



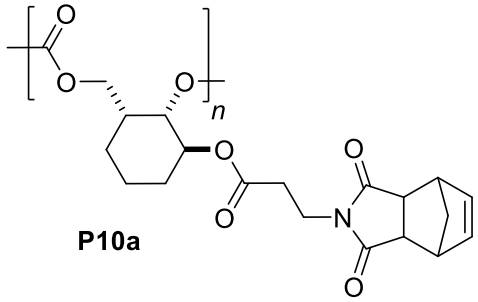
P8

P8 was obtained following the general procedure using monomer **8** (94 mg, 0.29 mmol), the reaction was also performed at 1.5 mmol scale (500 mg, 1.53 mmol). The conversions of **8** were determined by ^{1}H NMR at 90% and 93%, respectively. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.52 (1H), 7.95 – 7.82 (4H), 7.51 (2H), 5.39 – 4.91 (2H), 4.27 – 3.95 (2H), 2.47 (1H), 1.87 – 1.57 (6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.2, 155.0, 154.3, 135.5, 132.4, 131.1, 129.4, 128.2, 127.7, 127.2, 126.6, 125.2, 72.6, 70.1, 69.0, 68.0, 35.9, 29.7, 25.6, 23.4, 22.9, 19.7, 19.1. **IR** (neat) ν_{max} = 2939, 1746, 1715, 1224, 1193 cm^{-1}. **DSC**: T_g (º C) = 106; **TGA**: T_d^5 (º C) = 224. **GPC**: M_n = 3.24 kg/mol, M_w = 5.22 kg/mol, $Đ$ = 1.60.



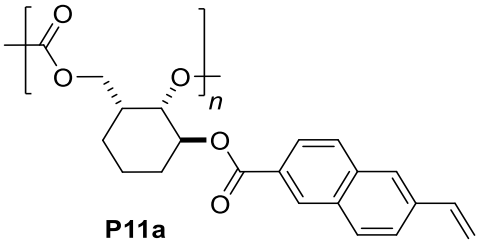
P9

P9 was obtained following the general procedure using monomer **9** (96 mg, 0.3 mmol). Conversion of **9** was determined by ^{1}H NMR at 84%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 7.29 – 7.26 (2H), 6.95 – 6.89 (3H), 4.84 (1H), 4.17 – 3.98 (4H), 3.61 - 3.54 (3H), 2.33 (1H), 1.86 (2H), 1.73 (3H), 1.58 – 1.51 (5H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.0, 129.4, 120.5, 114.5, 73.5, 68.8, 68.5, 67.5, 35.1, 26.7, 26.2, 26.2, 25.3, 23.1, 18.9. **IR** (neat) ν_{max} = 2939, 2867, 1742 (C=O), 1238 cm^{-1}. **DSC**: T_g (º C) = 15; **TGA**: T_d^5 (º C) = 301. **GPC**: M_n = 7.06 kg/mol, M_w = 10.20 kg/mol, $Đ$ = 1.44.



P10a

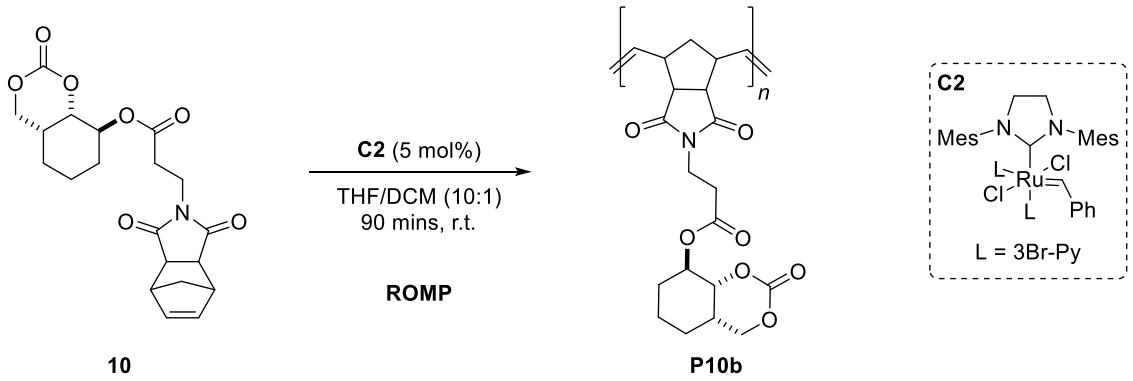
P10a was obtained following the general procedure using monomer **10** (112 mg, 0.29 mmol). Conversion of **10** was determined by ^{1}H NMR at 96%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 6.09 (2H), 5.04 – 4.99 (1H), 4.76 – 4.74 (1H), 4.15 – 3.94 (2H), 3.61 (2H), 3.36 (2H), 3.25 (2H), 2.49 – 2.48 (2H), 2.29 (1H), 1.77 – 1.52 (8H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 177.2, 177.2, 169.3, 169.1, 155.0, 154.2, 154.0, 134.4, 72.7, 72.3, 69.6, 68.7, 67.9, 52.1, 45.7, 44.9, 35.5, 34.0, 33.8, 33.7, 32.2, 32.0, 25.4, 23.1, 22.8, 18.9. **IR** (neat) ν_{max} = 2943, 1740, 1694, 1235 cm^{-1}. **DSC**: T_g (º C) = 120; **TGA**: T_d^5 (º C) = 315. **GPC**: M_n = 7.23 kg/mol, M_w = 9.63 kg/mol, $Đ$ = 1.33.



P11a

P11a was obtained following the general procedure using monomer **11** (106 mg, 0.3 mmol). Conversion of **11** was determined by ^{1}H NMR at 91%. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.46 (1H), 7.95 – 7.47 (5H), 6.82 (1H), 5.87 (1H), 5.36 – 5.04 (3H), 4.27 – 4.00 (2H), 2.77 – 2.48 (1H), 1.88 – 1.43 (6H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.1, 155.0, 154.4, 137.4, 136.6, 135.8, 132.1, 130.8, 129.6, 128.3, 127.1, 126.0, 125.6, 124.0, 115.6, 72.7, 68.9, 36.0, 25.6, 23.0, 19.2. **IR** (neat) ν_{max} = 2931, 2866, 1746 (C=O), 1714 (C=O), 1235 cm^{-1}. **DSC**: T_g (º C) = 156; **TGA**: T_d^5 (º C) = 221. **GPC**: M_n = 7.18 kg/mol, M_w = 11.46 kg/mol, $Đ$ = 1.59.

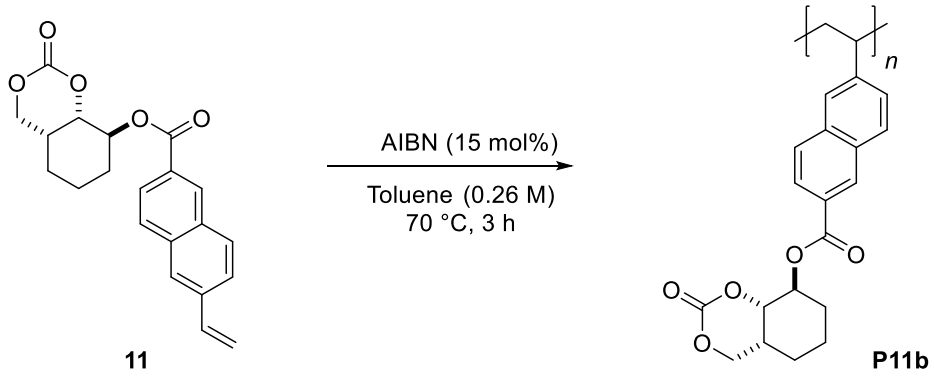
Procedure for ring opening metathesis polymerization



10 **P10b**

In a nitrogen-filled glovebox, to a solution of **10** (78 mg, 0.2 mmol, 1 equiv.) in THF (2 mL, 0.1 M) was added a freshly prepared solution of **C2** (9 mg, 0.01 mmol, 5 mol%) in DCM (0.2 mL, 50 μM). The reaction mixture was stirred at room temperature for 1 h and 30 minutes. Hereafter, the mixture was quenched with ethyl vinyl ether (1 mL). A sample was taken to determine the conversion of **10** by ^{1}H NMR ($CDCl_3$) which was determined at 96%. Precipitation from MeOH provided the polymer as a white powder. The supernatant was removed, the residue was dissolved in $CHCl_3$ and reprecipitated with MeOH. The white powder produced was collected and dried in high vacuum. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 5.69 – 5.45 (2H), 5.03 (1H), 4.67 (2H), 4.19 (1H), 3.74 (2H), 3.21 (2H), 2.91 (1H), 2.59 (2H), 2.31 (1H), 1.83 – 1.35 (9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 176.4, 175.9, 169.6, 148.2, 148.0, 129.5, 128.5, 128.4, 75.3, 72.5, 68.8, 48.9, 45.3, 40.2, 34.8, 33.2, 28.2, 24.3, 22.2, 18.6. **IR** (neat) ν_{max} = 2936, 1744 (C=O), 1695 (C=O) cm^{-1}. **DSC**: T_g (º C) = 156; **TGA**: T_d^5 (º C) = 242. **GPC**: M_n = 4.12 kg/mol, M_w = 4.56 kg/mol, $Đ$ = 1.10.

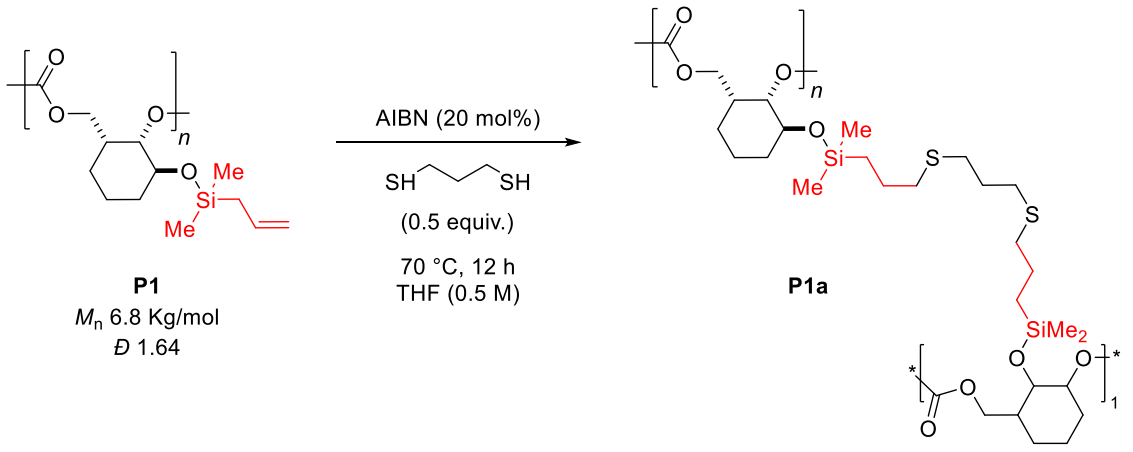
Procedure for the radical polymerization of 11



11 **P11b**

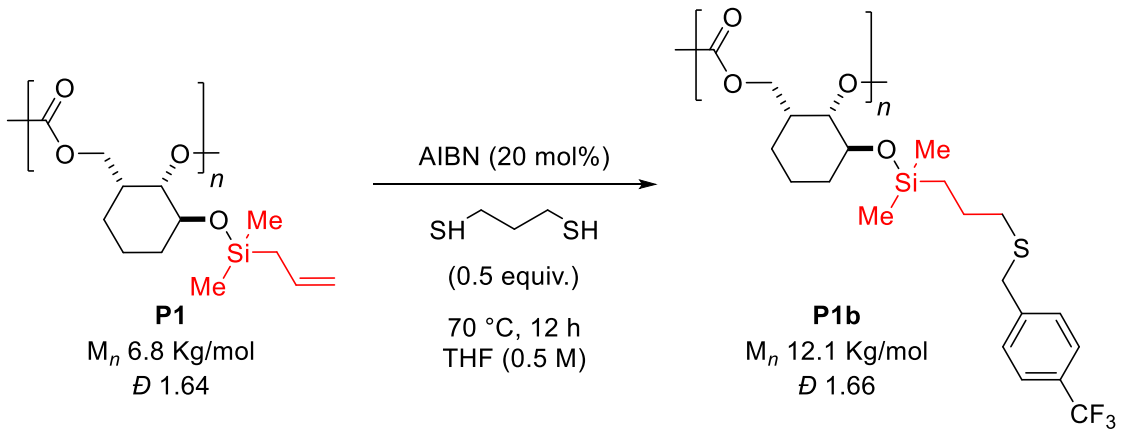
In a nitrogen-filled glovebox, a vial equipped with a stirring bar was charged with **11** (70 mg, 0.26 mmol, 1 equiv) followed by dry and degassed toluene (0.8 mL, 0.25 M). Then 200 μL of a freshly prepared solution of AIBN (10 mg, 0.06 mmol, 15 mol%) in toluene (300 μL, 0.2 M) was added. The reaction mixture was stirred at room temperature for 3 h at 70 °C. The reaction mixture was then quenched by the addition of MeOH. The conversion of **11** was determined by ^{1}H NMR ($CDCl_3$) to be >98%. The resulting white precipitate was collected as pure polymer **P11b**, and dried in vacuo. **^{1}H NMR** (300 MHz, $CDCl_3$) δ 8.55 (1H), 7.98 – 7.85 (4H), 7.54 (2H), 5.34 (1H), 5.03 (1H), 4.20 (2H), 2.53 (1H), 1.86 – 1.53 (8H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 165.3, 154.3, 135.6, 132.4, 131.2, 129.4, 128.2, 127.7, 127.2, 126.7, 125.2, 92.3, 72.6, 69.1, 68.0, 35.9, 26.0, 25.6, 23.5, 22.9, 19.1. **IR** (neat) ν_{max} = 2937, 1743 (C=O), 1714 (C=O), 1249, 1224 cm^{-1}. **DSC**: T_g (º C) = 95; **TGA**: T_d^5 (º C) = 257. **GPC**: M_n = 4.47 kg/mol, M_w = 7.04 kg/mol, $Đ$ = 1.57.

Procedure for post-polymerization modifications



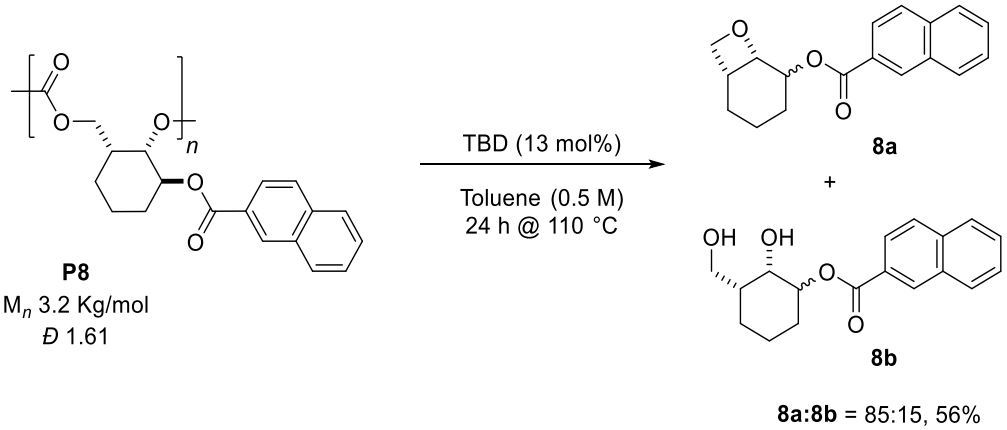
M_n 6.8 Kg/mol
$Đ$ 1.64

To a solution of **P1** (45 mg, 0.16 mmol, 1 equiv) in dry THF (0.3 mL, 0.5 M) under nitrogen was added 1,3-propanedithiol (8 µL, 0.08 mmol, 0.50 equiv) followed by AIBN (5.3 mg, 0.032 mmol, 20 mol%). The resulting mixture was then stirred at 70 °C for 12 h. The volatiles were removed in vacuo, and the crude reaction product was washed three times with methanol. The resulting purified polymer **P1a** was insoluble either in THF and $CDCl_3$, it was therefore characterized only through DSC, TGA and IR. **IR** (neat) ν_{max} = 2936, 2665, 1741 (C=O), 1237 cm^{-1}. **DSC**: T_g (º C) = 32; **TGA**: T_d^5 (º C) = 326.



To a solution of **P1** (45 mg, 0.16 mmol, 1 equiv) in dry THF (0.3 mL, 0.5 M) under nitrogen was added 3-(trifluoromethyl)benzyl mercaptan (61.5 mg, 0.32 mmol, 2 equiv) followed by AIBN (5.3 mg, 0.032 mmol, 20 mol%). The resulting mixture was then stirred at 75 °C for 10 h. The volatiles were removed in vacuo, and the crude product was washed three times with methanol. The purified polymer **P1b** was then collected and dried in high vacuum. **^{1}H NMR** (300 MHz, CDCl3) δ 7.59 – 7.41 (4H), 4.61 (1H), 4.09 – 3.91 (3H), 3.75 (2H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.35 – 2.09 (1H), 1.84 (1H), 1.67 – 1.47 (9H), 0.68 – 0.63 (1H), 0.15 – 0.10 (6H). **^{13}C NMR** (75 MHz, $CDCl_3$) δ 155.2, 154.7, 139.9, 138.3, 132.7, 132.2, 131.0, 130.6, 129.1, 128.9, 126.1, 125.9, 125.5, 123.8, 122.3, 68.2, 66.6, 42.5, 36.7, 35.9, 35.0, 34.8, 29.2, 25.1, 23.2, 19.1, 18.5, 16.2, -1.6, -1.9. **^{19}F NMR** (282 MHz, $CDCl_3$) δ 62.7. **IR** (neat) ν_{max} = 2941, 1742 (C=O), 1449, 1329, 1250 cm^{-1}. **DSC**: *T*g (º C) = -12; **TGA**: T_d^5 (º C) = 251. **GPC**: M_n = 1.21 kg/mol, M_w = 2.02 kg/mol, *Đ* = 1.66.

Procedure of TBD-catalyzed polymer degradation of P8



In a nitrogen-filled glovebox, a vial equipped with a stirring bar was charged with **P8** (50 mg, 0.15 mmol carbonate repeat units) followed by a freshly prepared solution of TBD (3.5 mg, 0.02 mmol, 13 mol%) in toluene (0.3 mL, [M] = 0.50), transferred into a closed vial (10 mL), and placed in an oil bath heated to 110 °C for 24 h. The reaction mixture was allowed to cool to room temperature and the crude product purified through column chromatography to afford **8a** and **8b** as an inseparable 85:15 mixture in 56% yield (17 mg). **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 1.6 Hz, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.98 – 7.96 (m, 1H), 7.90 – 7.87 (m, 2H), 7.60 – 7.54 (m, 2H), 4.45 (dd, *J* = 11.0, 5.6 Hz, 1H), 4.37 (dd, *J* = 11.0, 7.8 Hz, 1H), 3.24 (dt, *J* = 4.1, 2.1 Hz, 1H), 3.19 (d, *J* = 3.9 Hz, 1H), 2.43 (ddt, *J* = 11.3, 7.8, 5.9 Hz, 1H), 2.16 – 2.12 (m, 1H), 1.79 – 1.70 (m, 2H), 1.49 – 1.44 (m, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.7, 135.6, 132.5, 131.1, 129.3, 128.3, 128.2, 127.8, 127.2, 126.7, 125.1, 66.7, 53.6, 52.5, 34.4, 24.7, 24.0, 16.9. (**8a**) **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{18}NaO_3$: 305.1148; found: 305.1159. (**8b**) **HRMS** (ESI): m/z $[M+Na]^+$ calcd for $C_{18}H_{20}NaO_4$: 323.1254; found: 323.1252. **IR** (neat) ν_{max} = 3507, 2936, 1714 (C=O), 1279, 1196 cm^{-1}.

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Copies of NMR and IR spectra

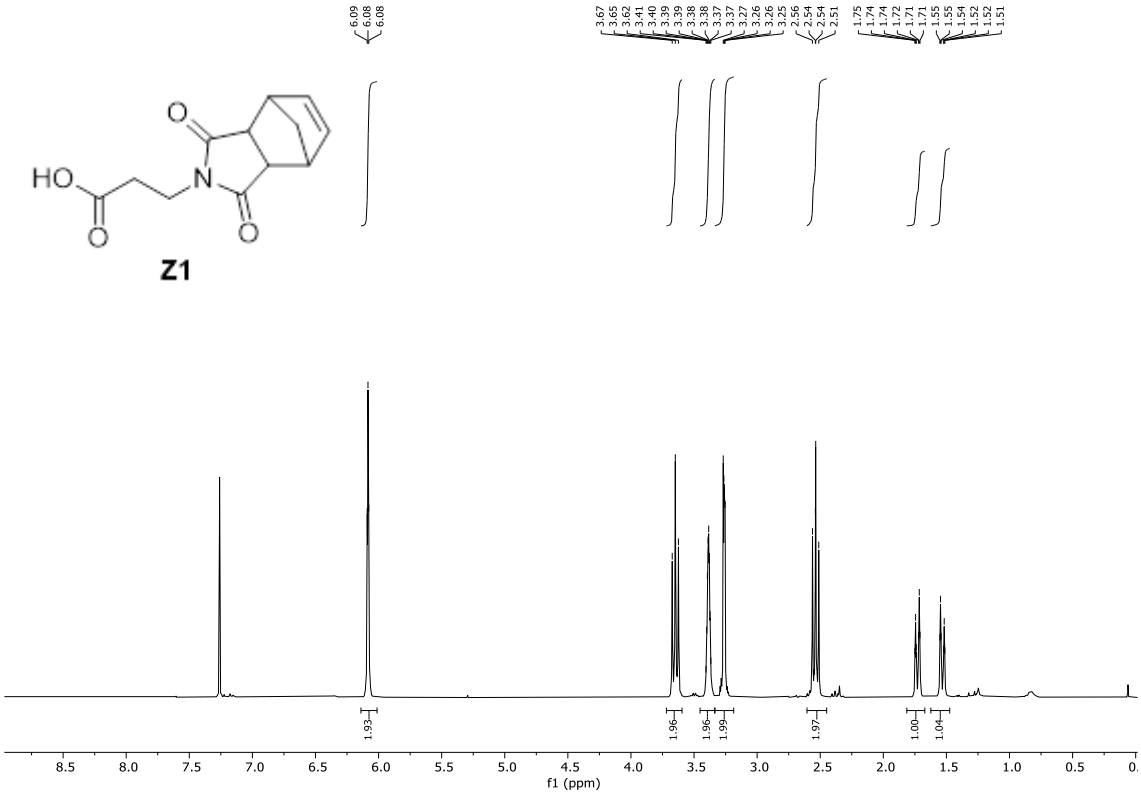


Figure S1: **^{1}H NMR** ($CDCl_3$, 300 MHz) of **Z1**

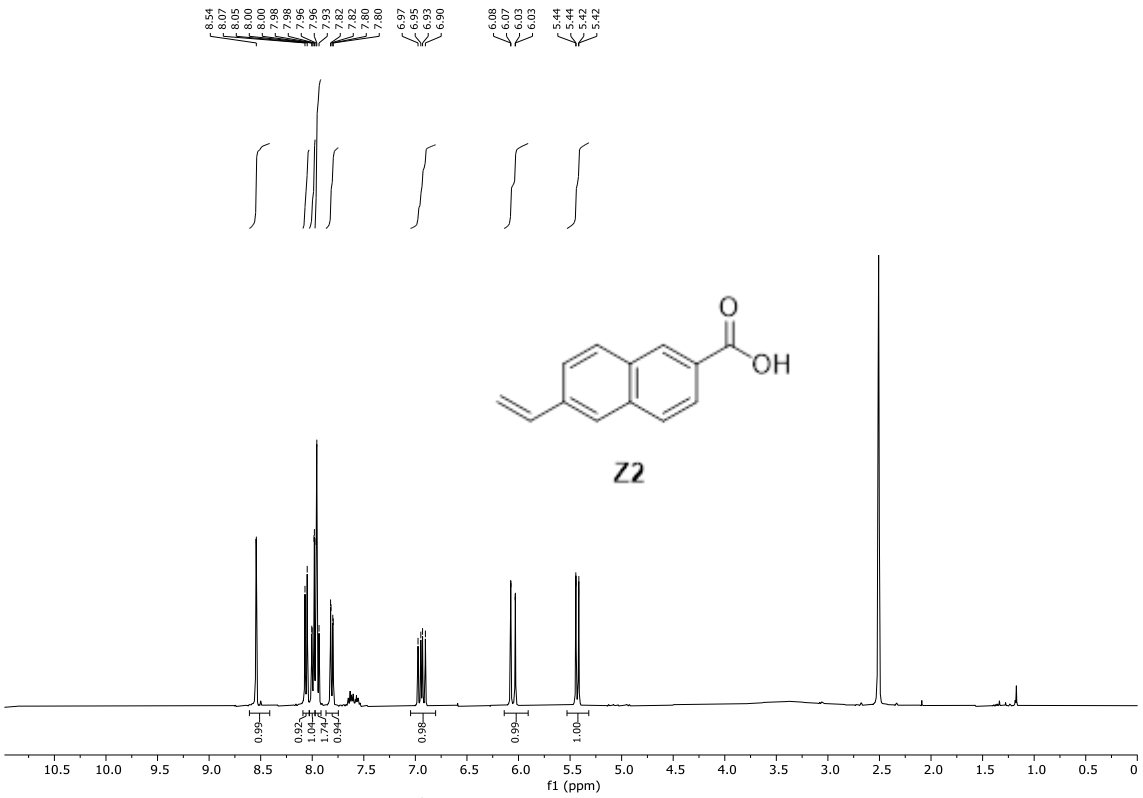


Figure S2: **^{1}H NMR** (DMSO, 400 MHz) of **Z2**

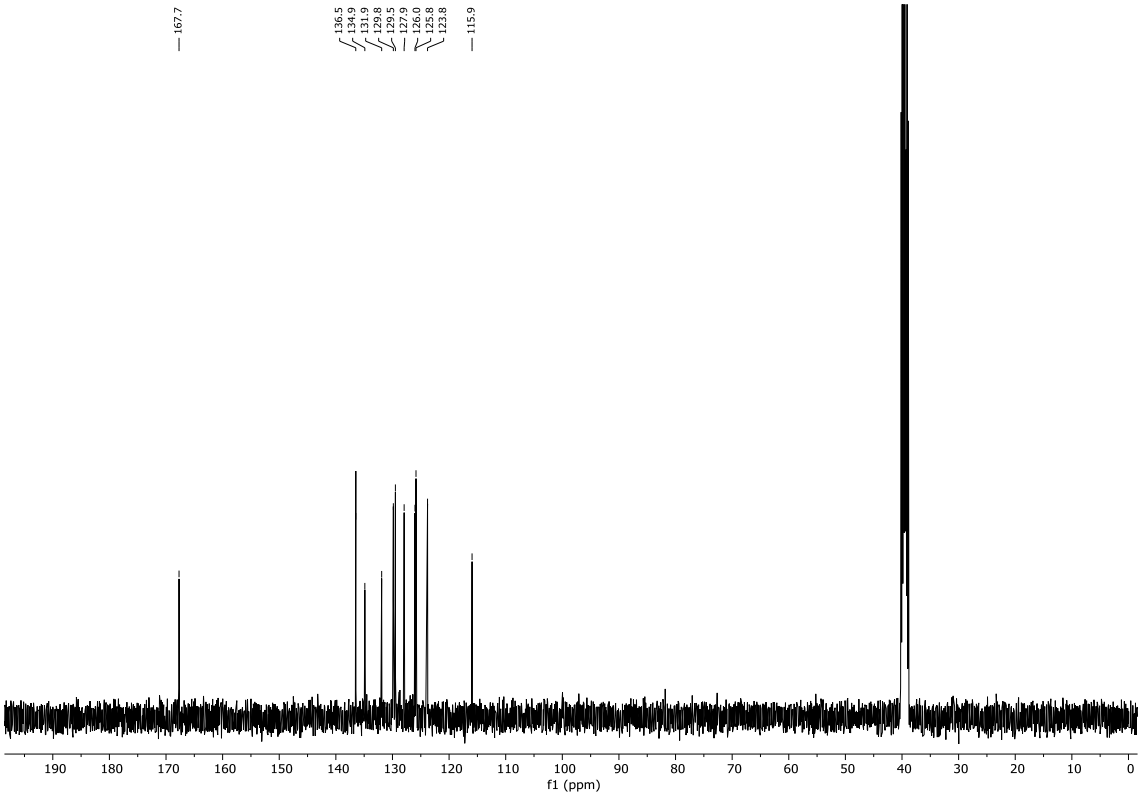


Figure S3: **^{13}C NMR** (DMSO, 101 MHz) of **Z2**

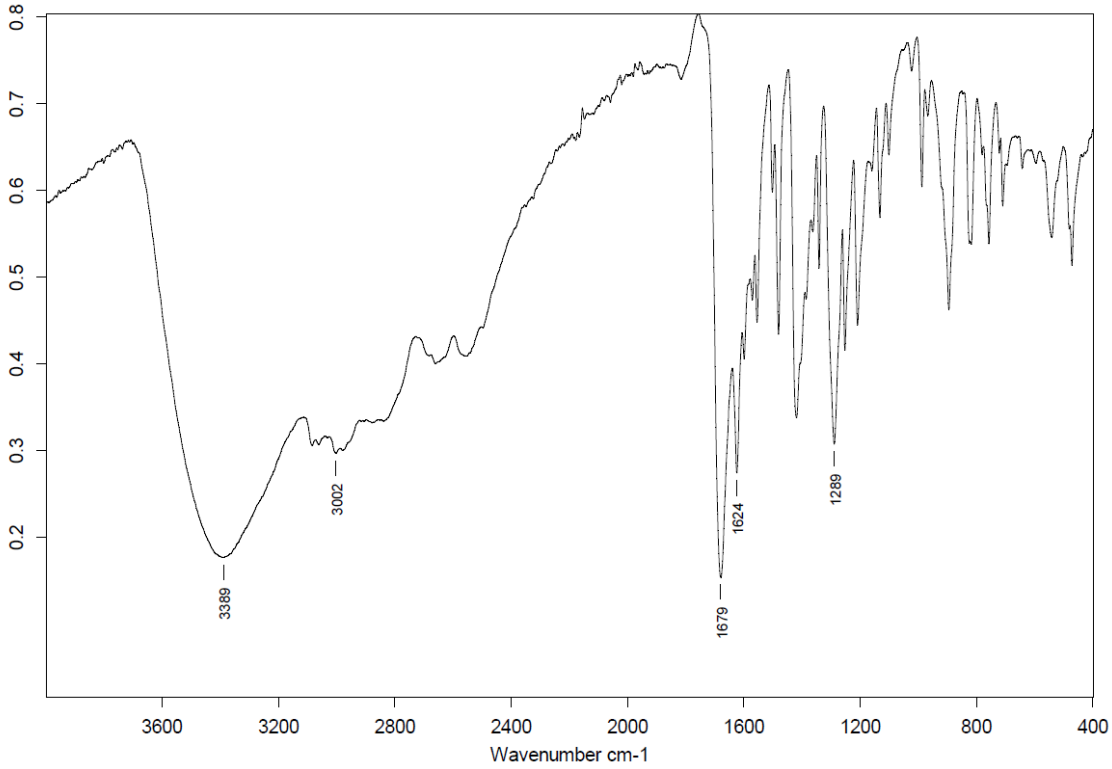


Figure S4: IR spectrum (neat) of **Z2**

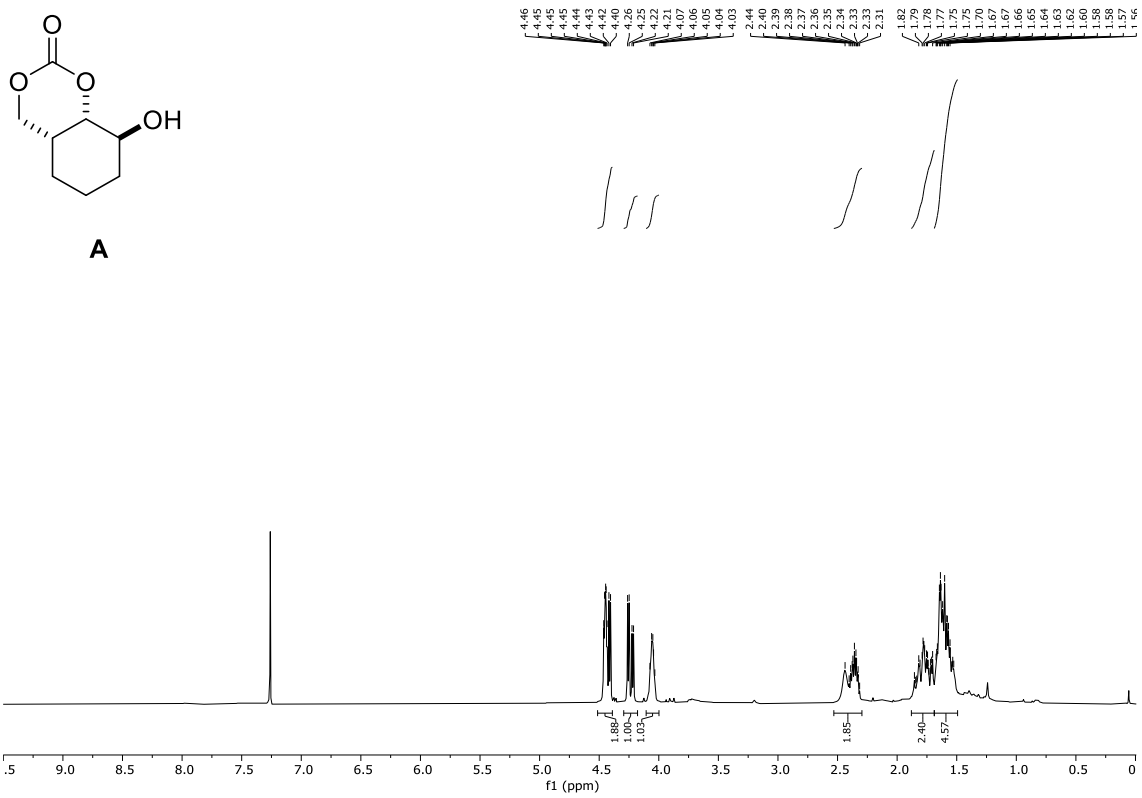


Figure S5: **^{1}H NMR** ($CDCl_3$, 300 MHz) of **A**

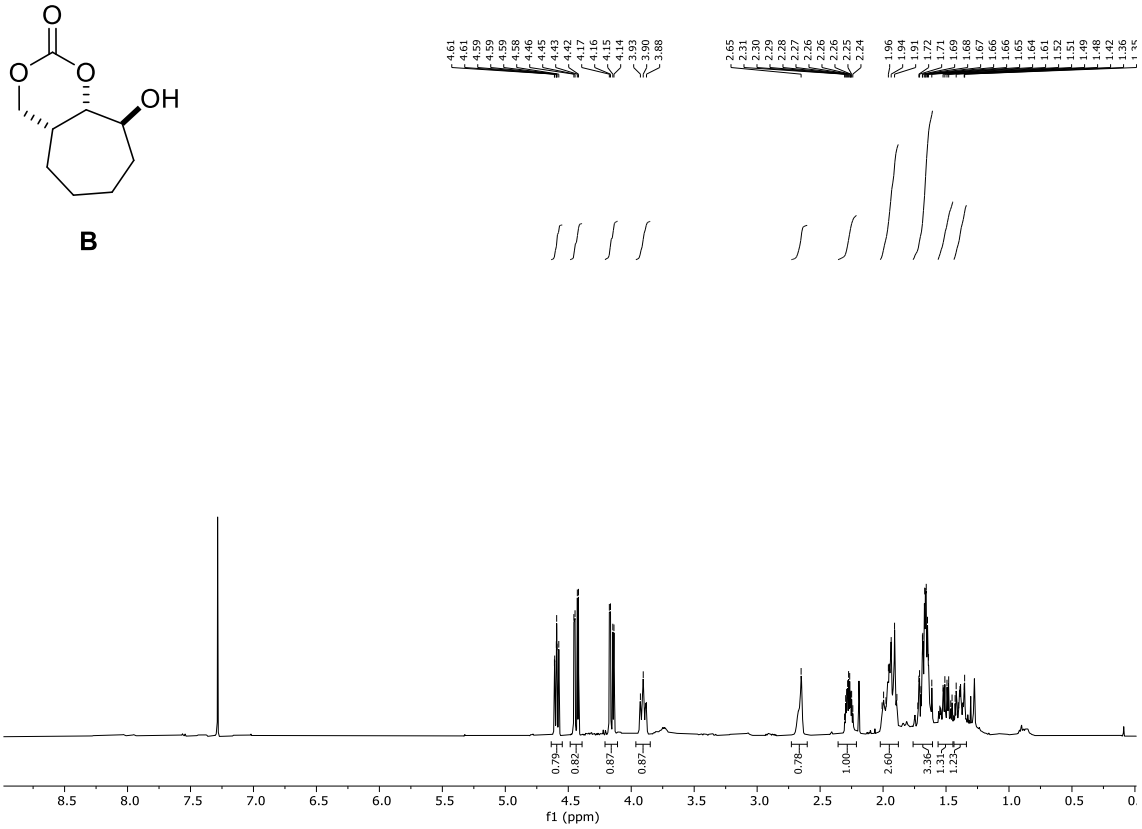


Figure S6: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **B**

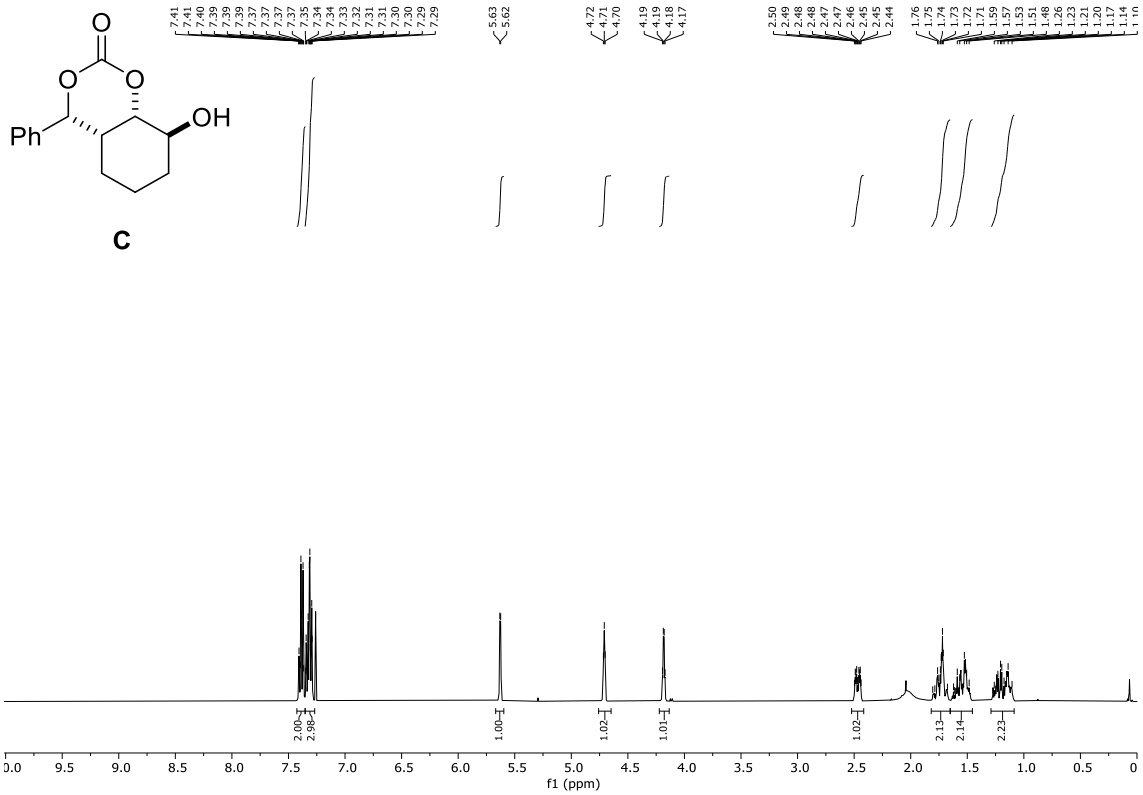


Figure S7: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **C**

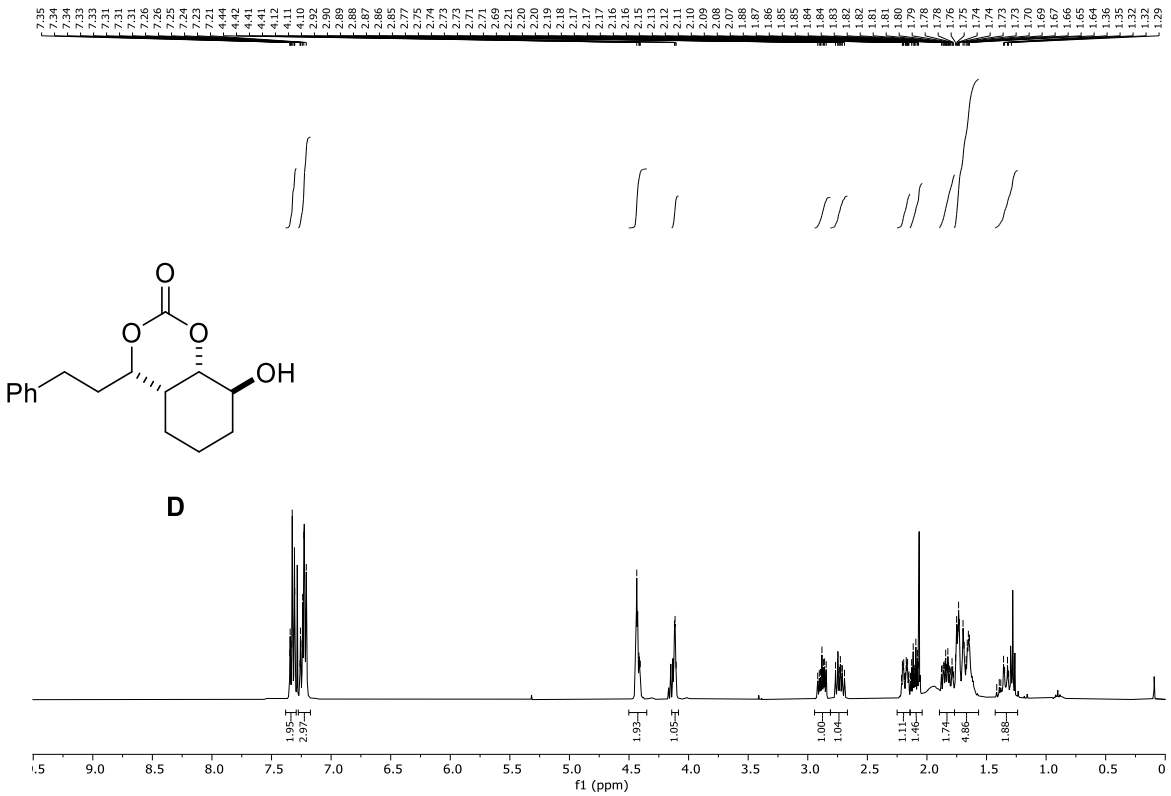


Figure S8: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **D**

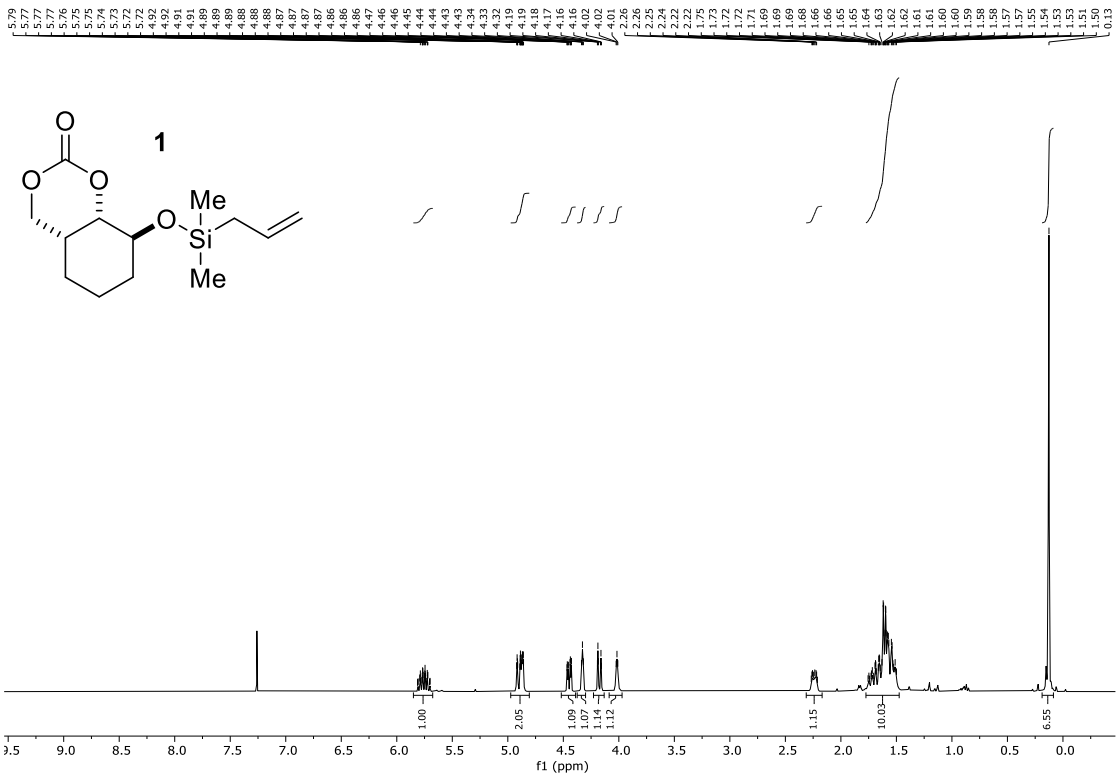


Figure S9: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **1**

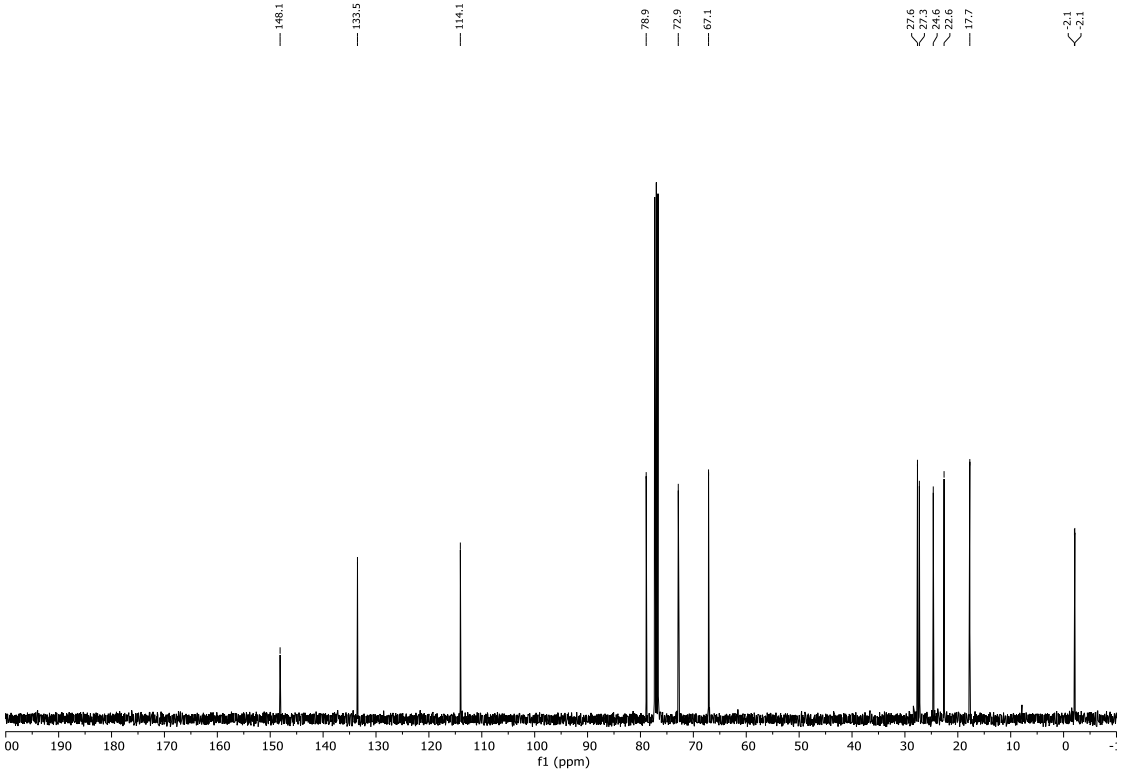


Figure S10:**^{13}C NMR** ($CDCl_3$, 101 MHz) of **1**

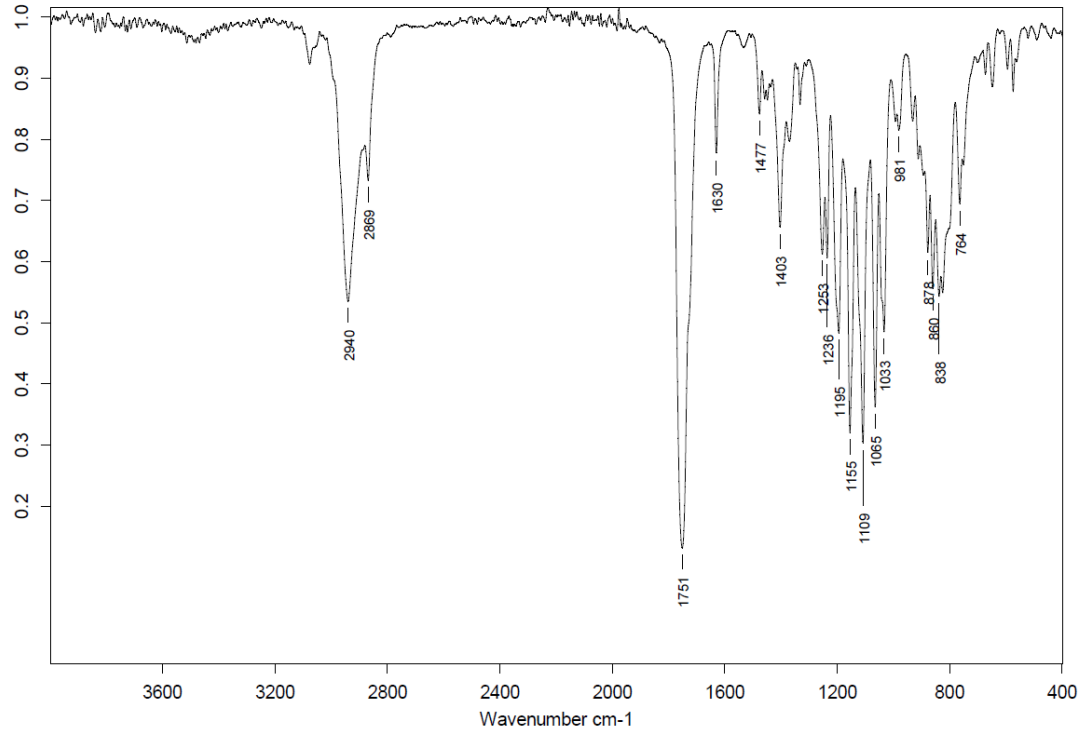


Figure S11: IR spectrum (neat) of **1**

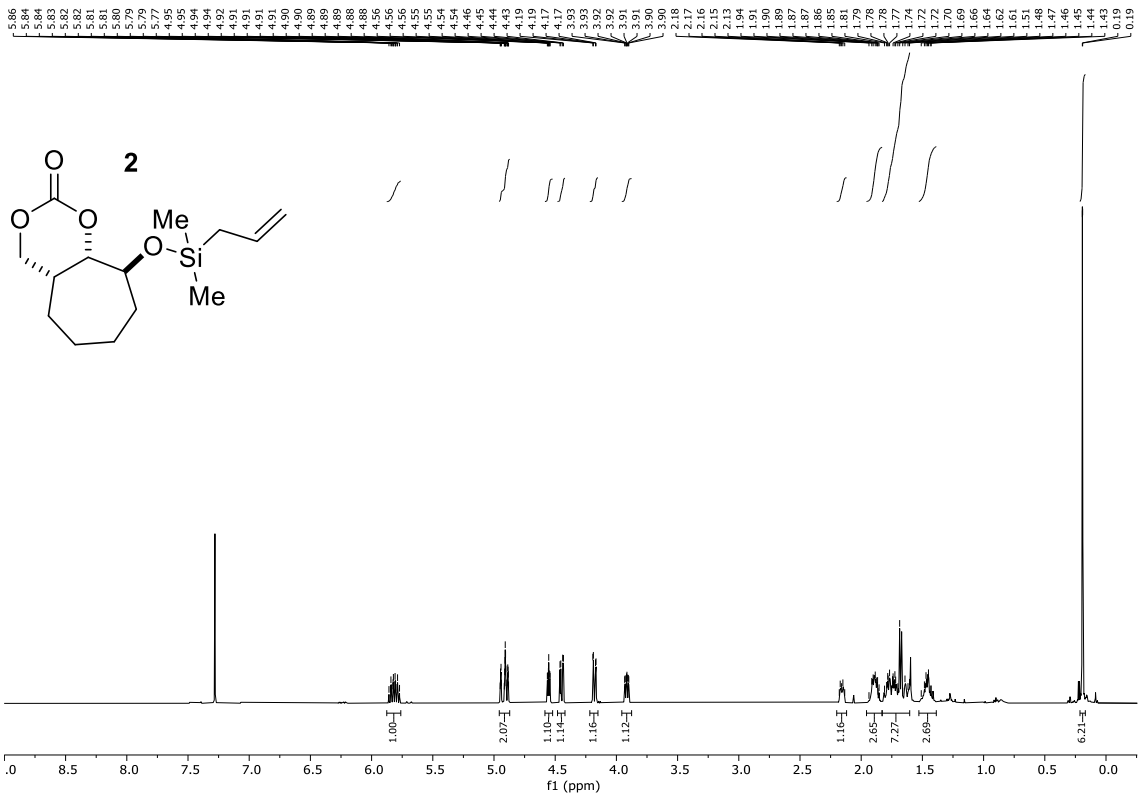


Figure S12: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **2**

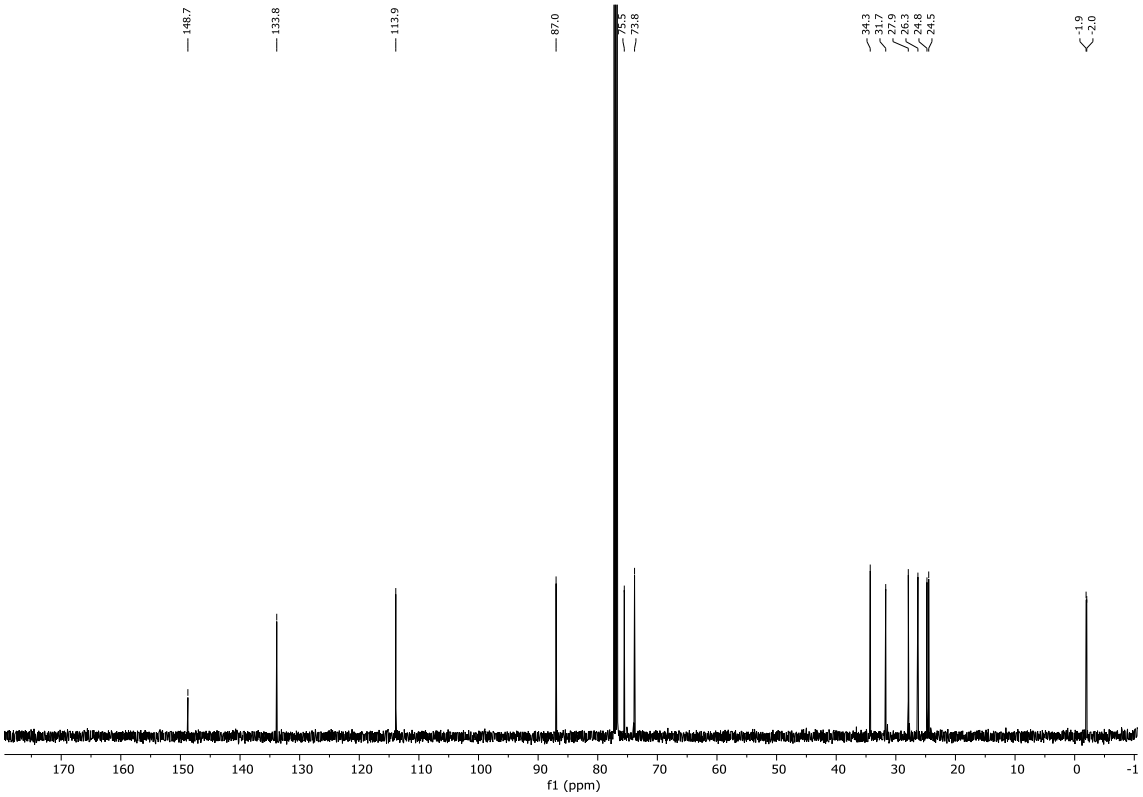


Figure S13: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **2**

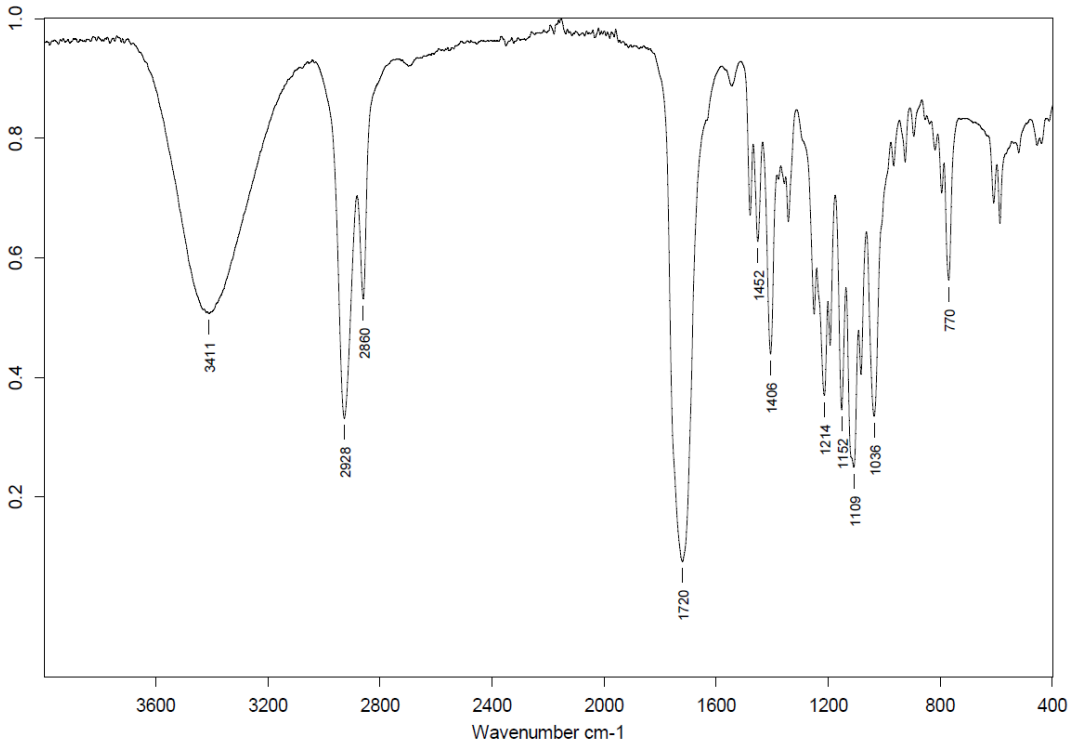


Figure S14: IR spectrum (neat) of **2**

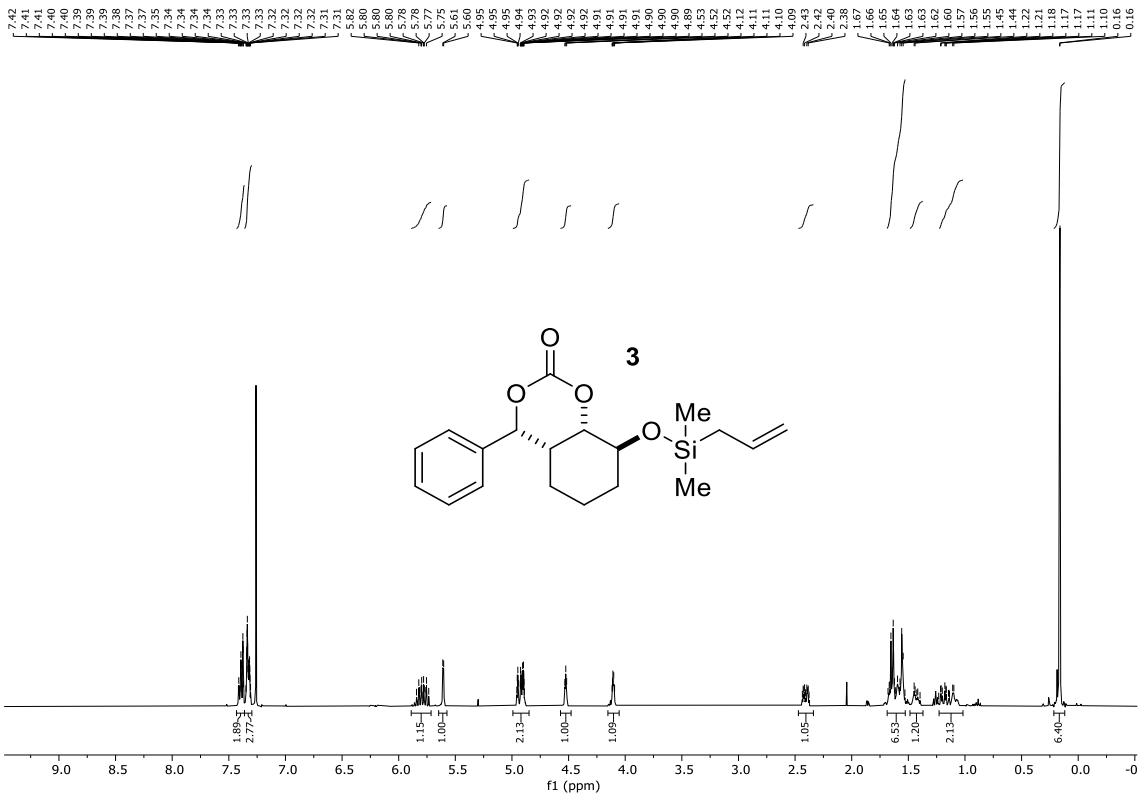


Figure S15: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **3**

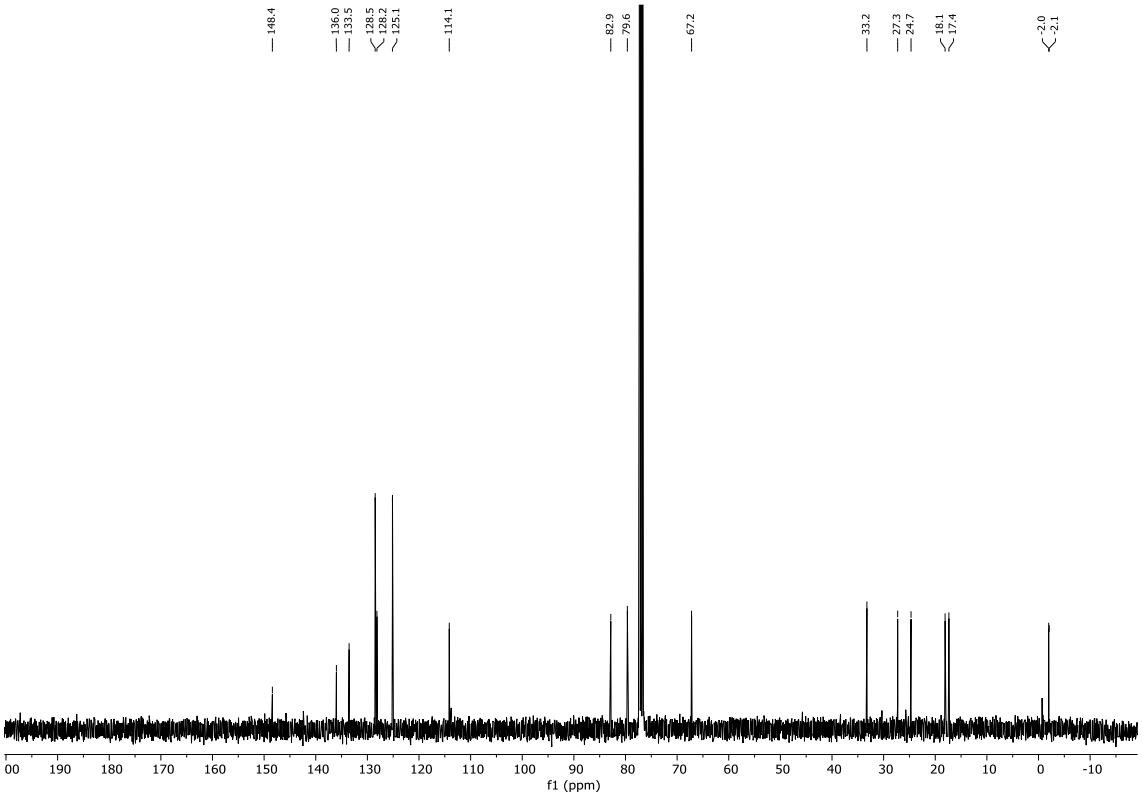


Figure S16:**^{13}C NMR** ($CDCl_3$, 101 MHz) of **3**

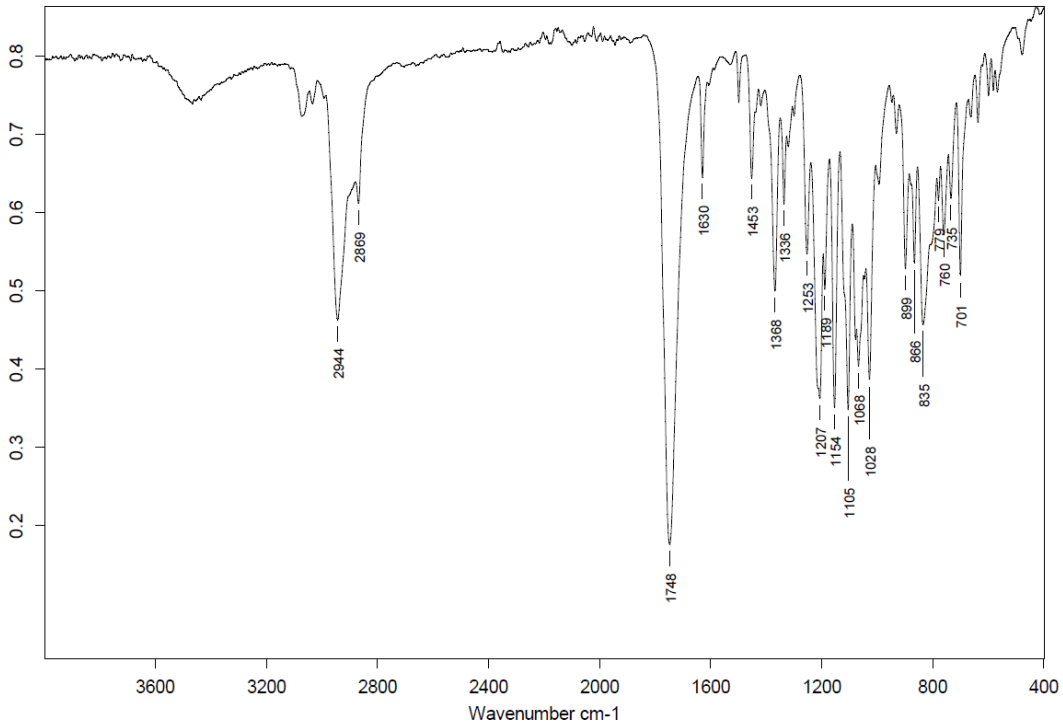


Figure S17: IR spectrum (neat) of **3**

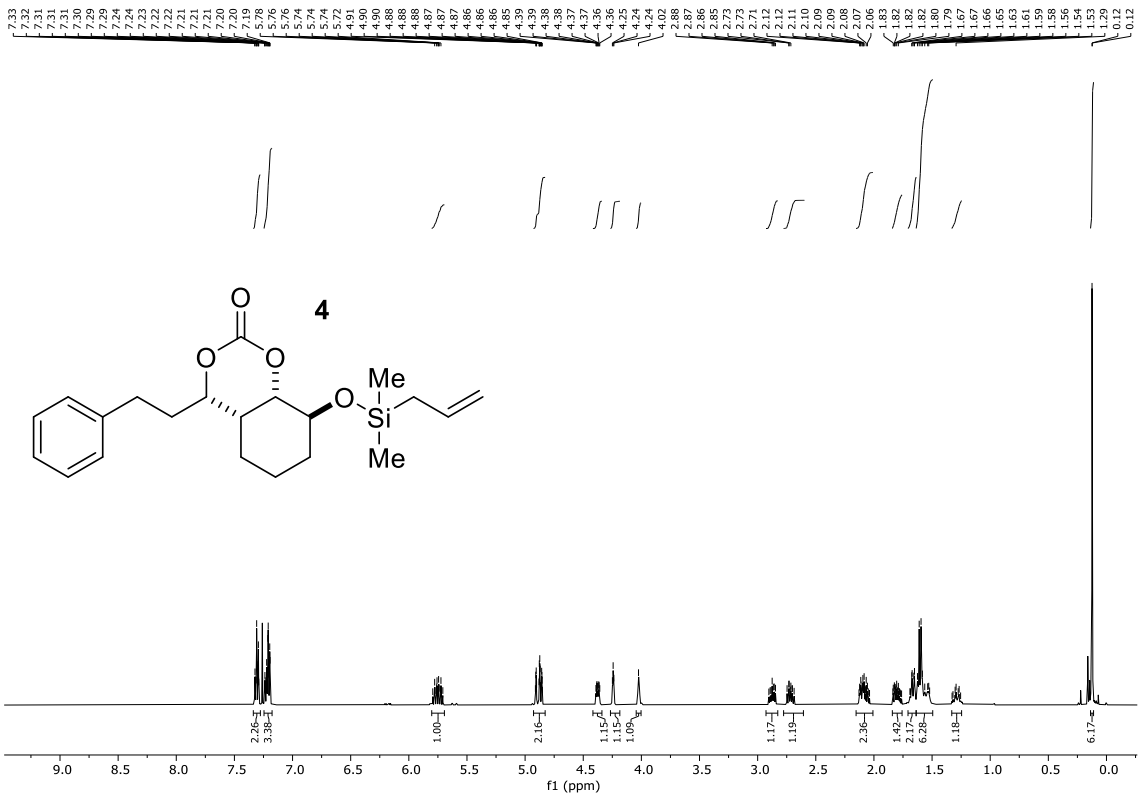


Figure S18: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **4**

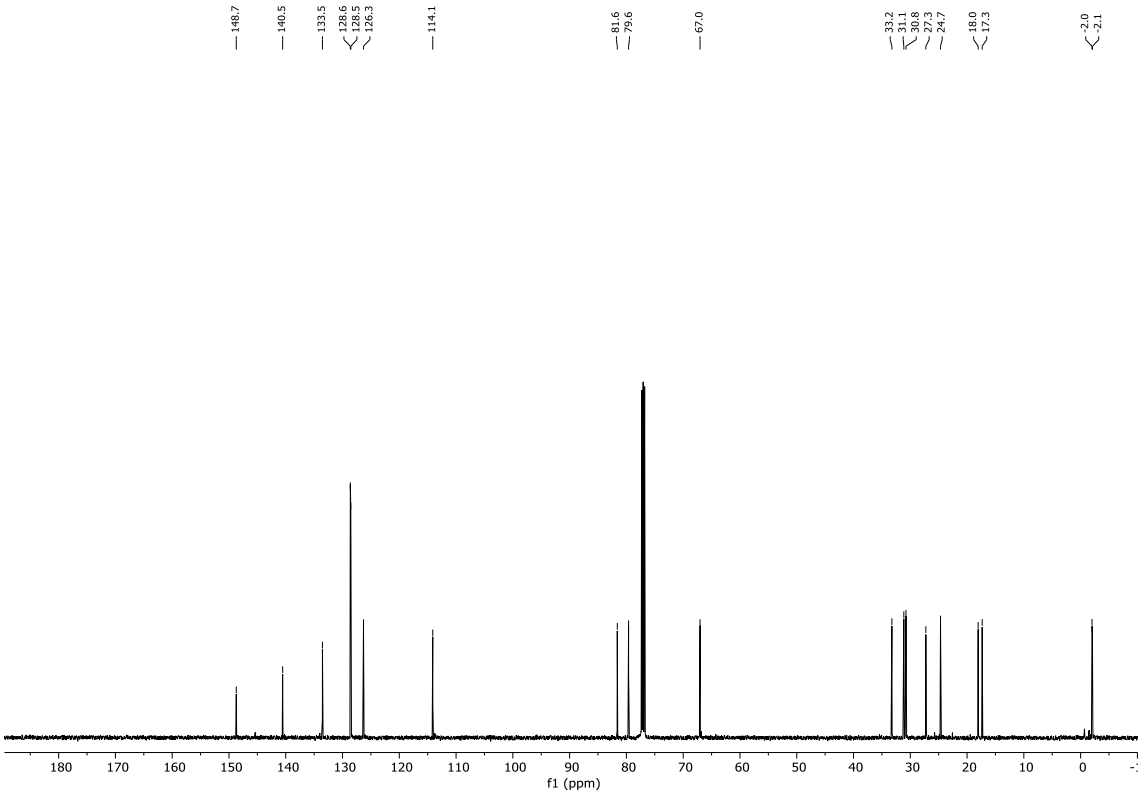


Figure S19: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **4**

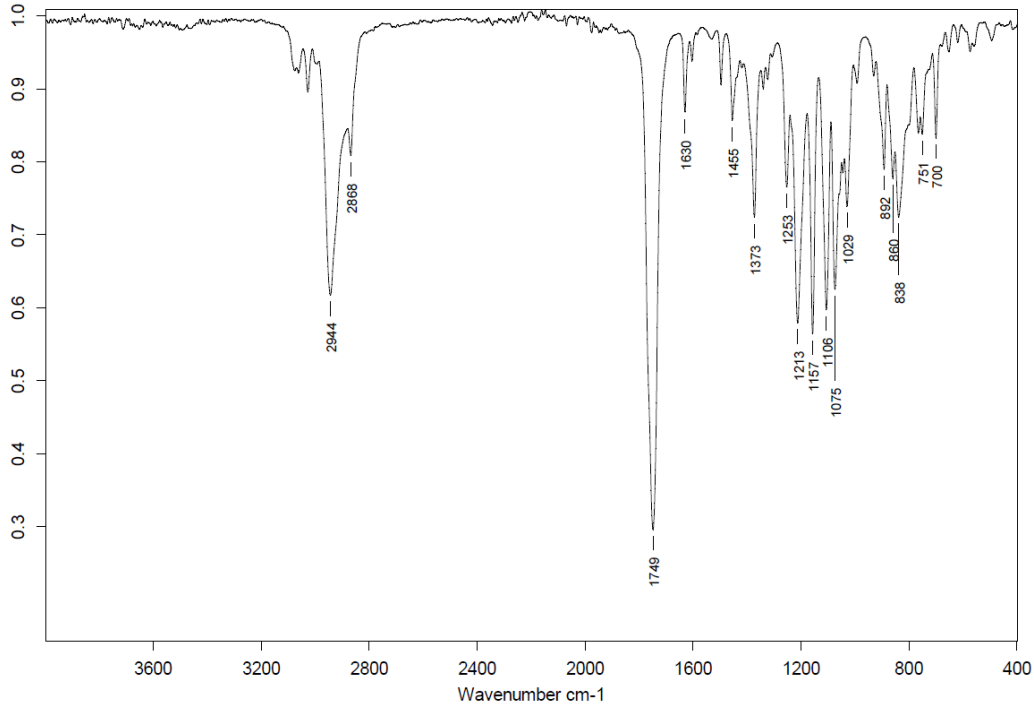


Figure S20: IR spectrum (neat) of **4**

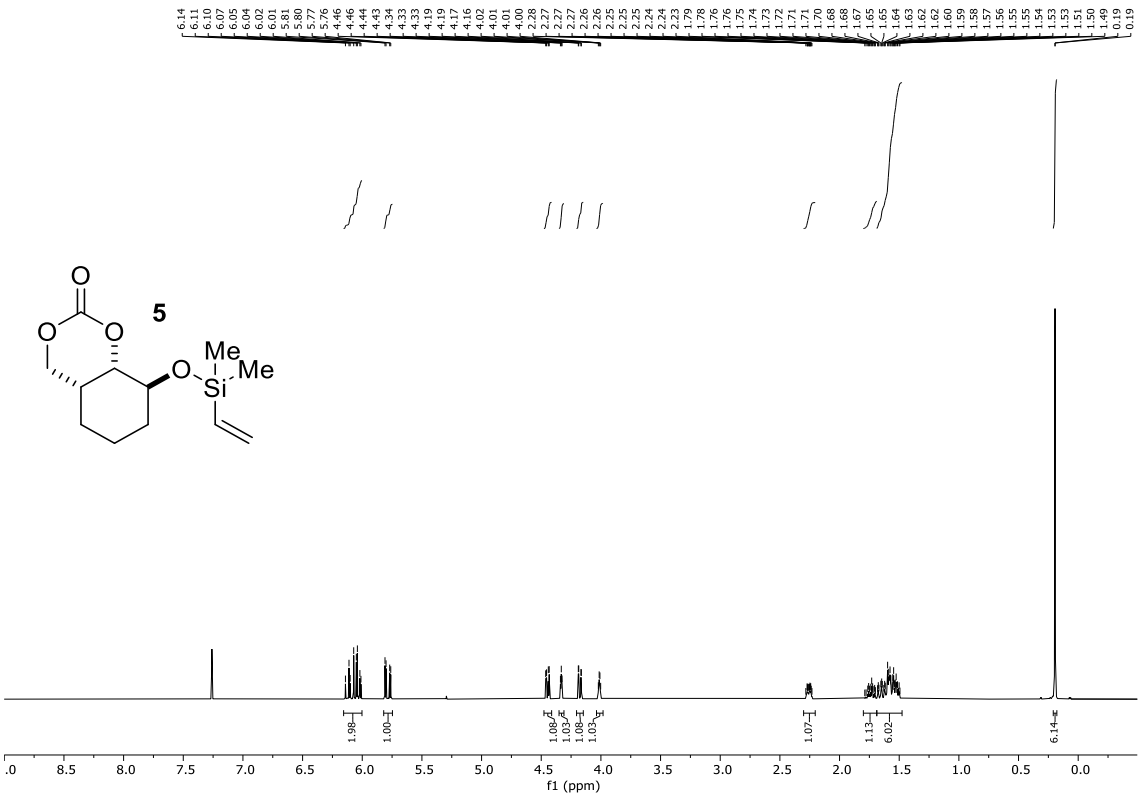


Figure S21: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **5**

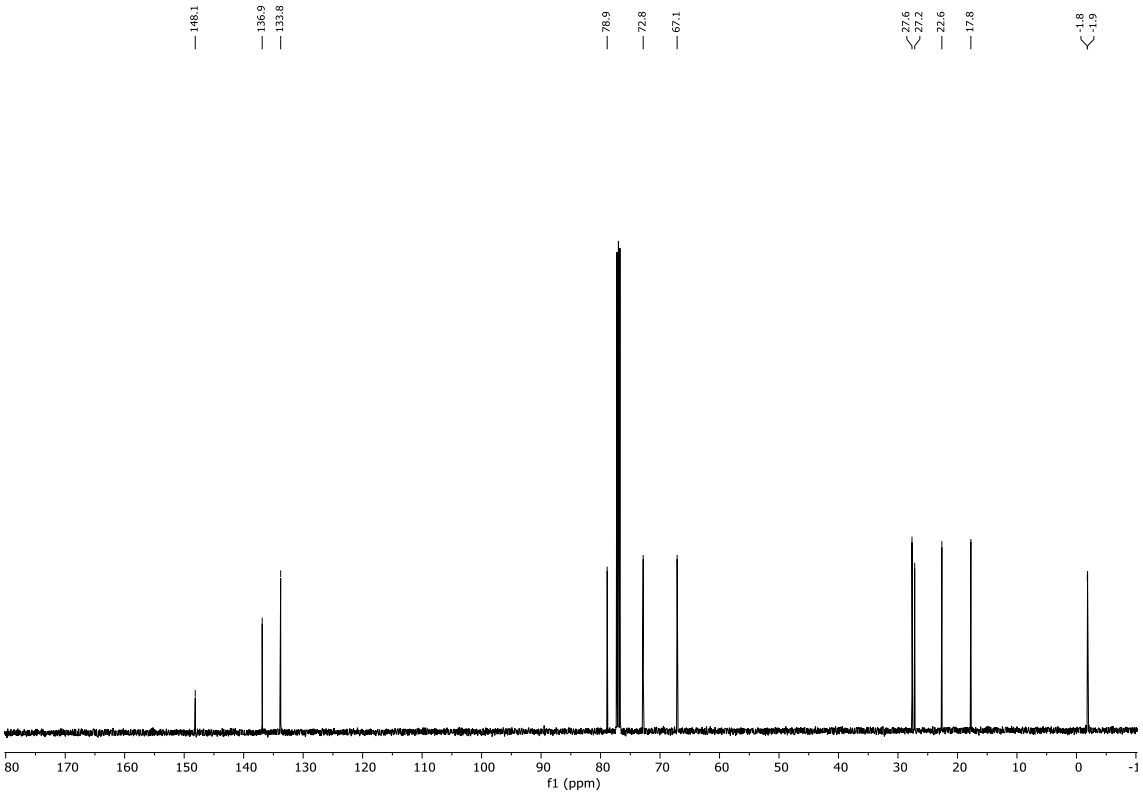


Figure S22: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **5**

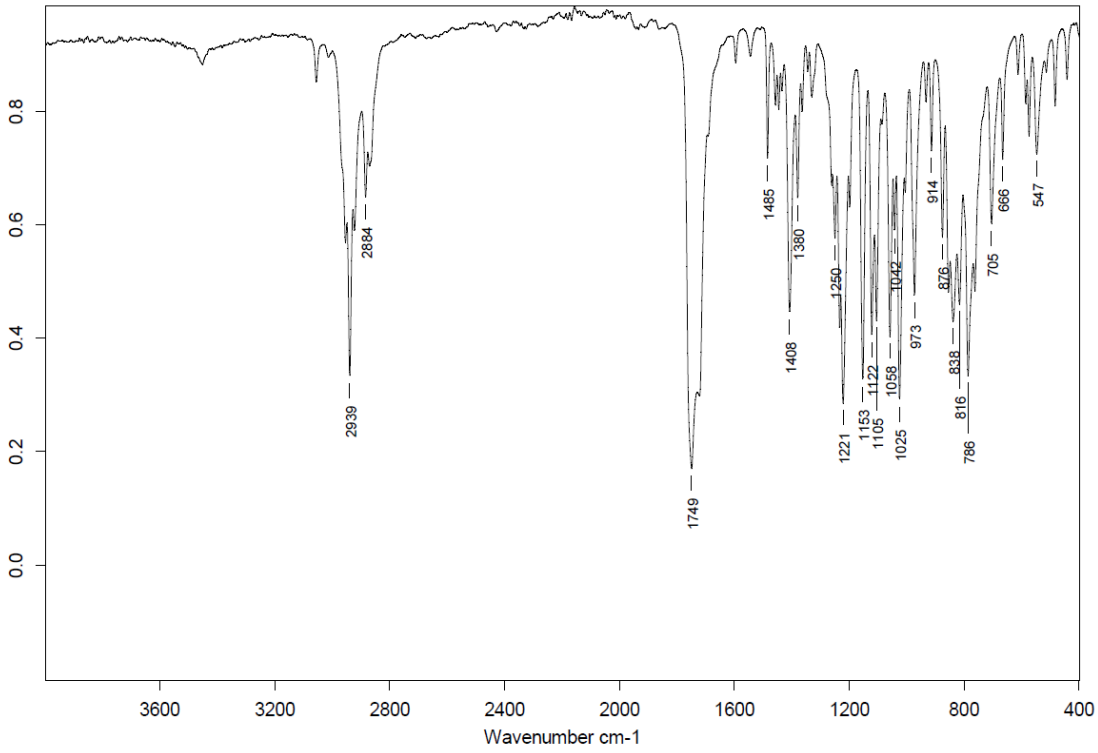


Figure S23: IR spectrum (neat) of **5**

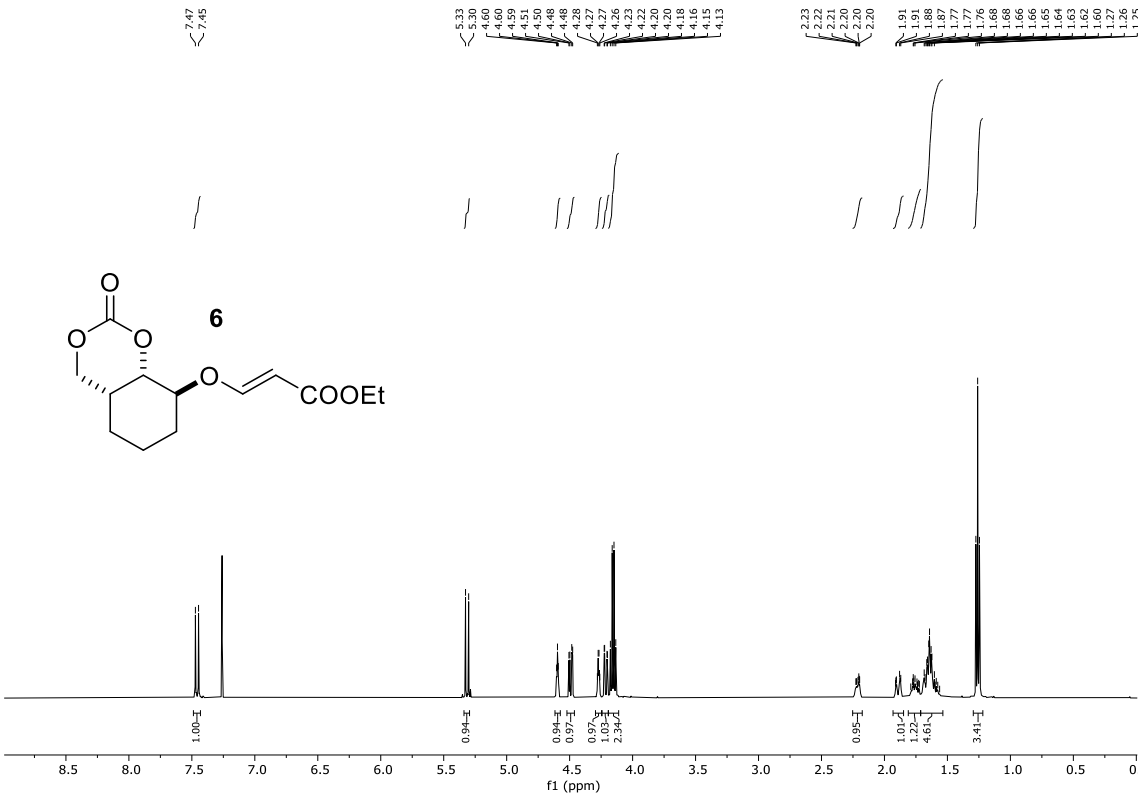


Figure S24: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **6**

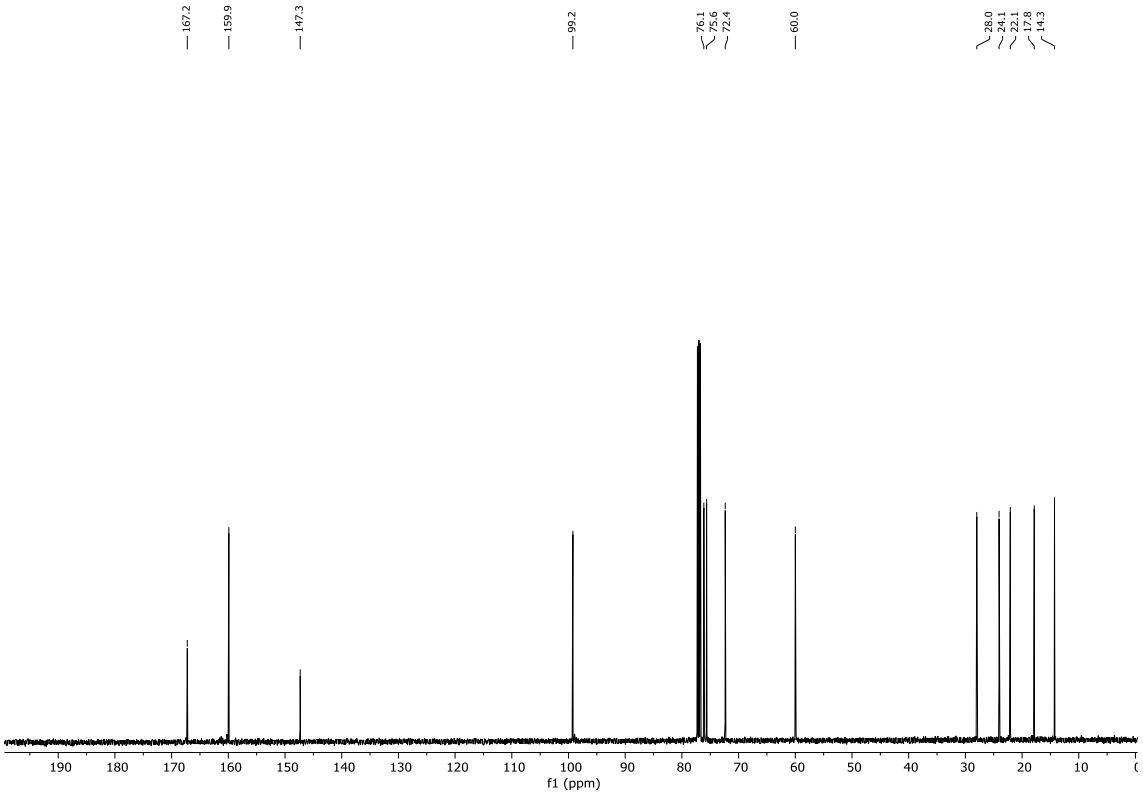


Figure S25:**^{13}C NMR** ($CDCl_3$, 126 MHz) of **6**

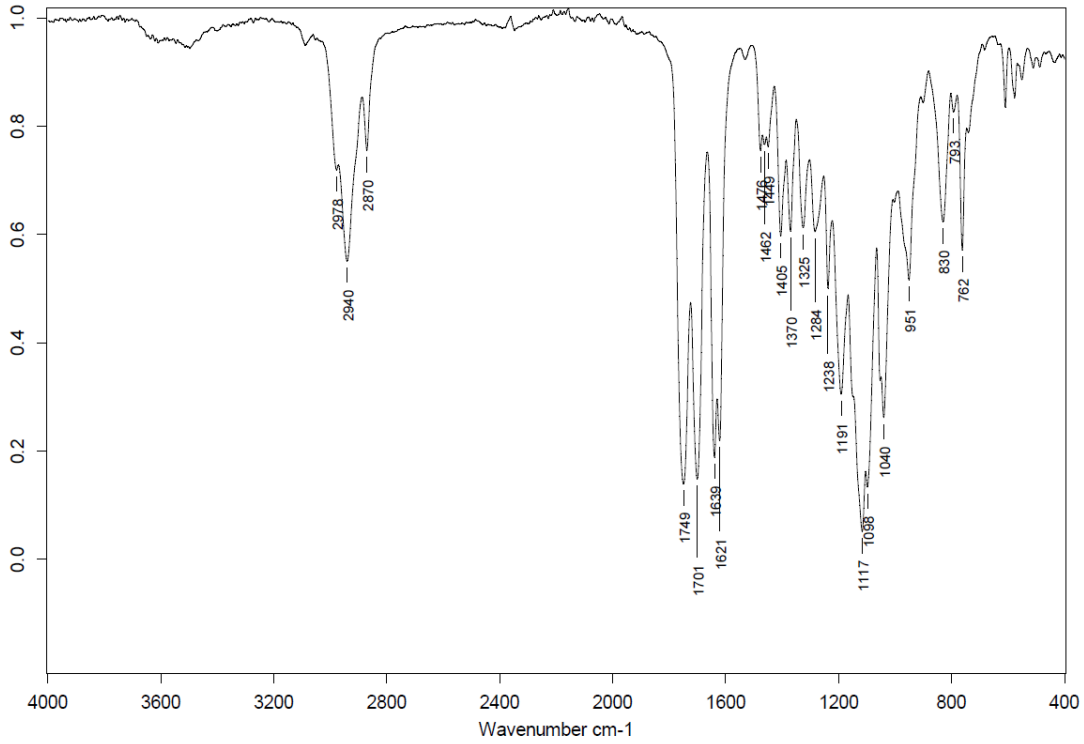


Figure S26: IR spectrum (neat) of **6**

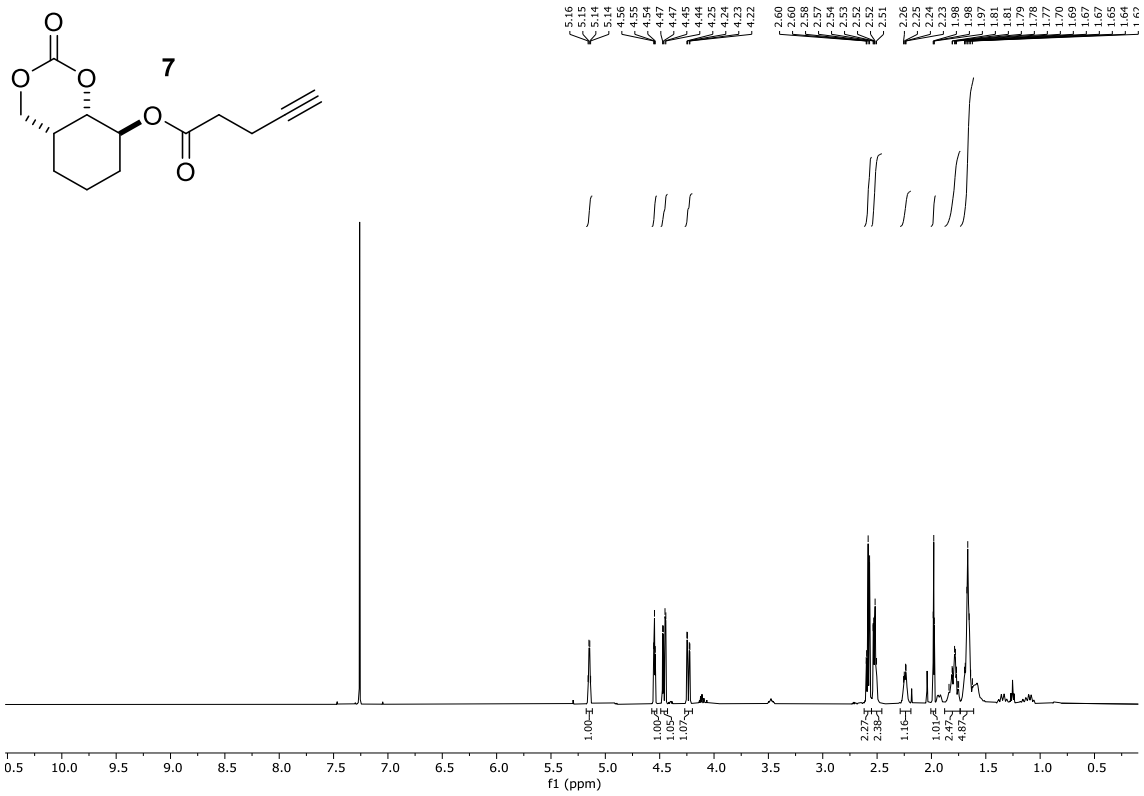


Figure S27: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **7**

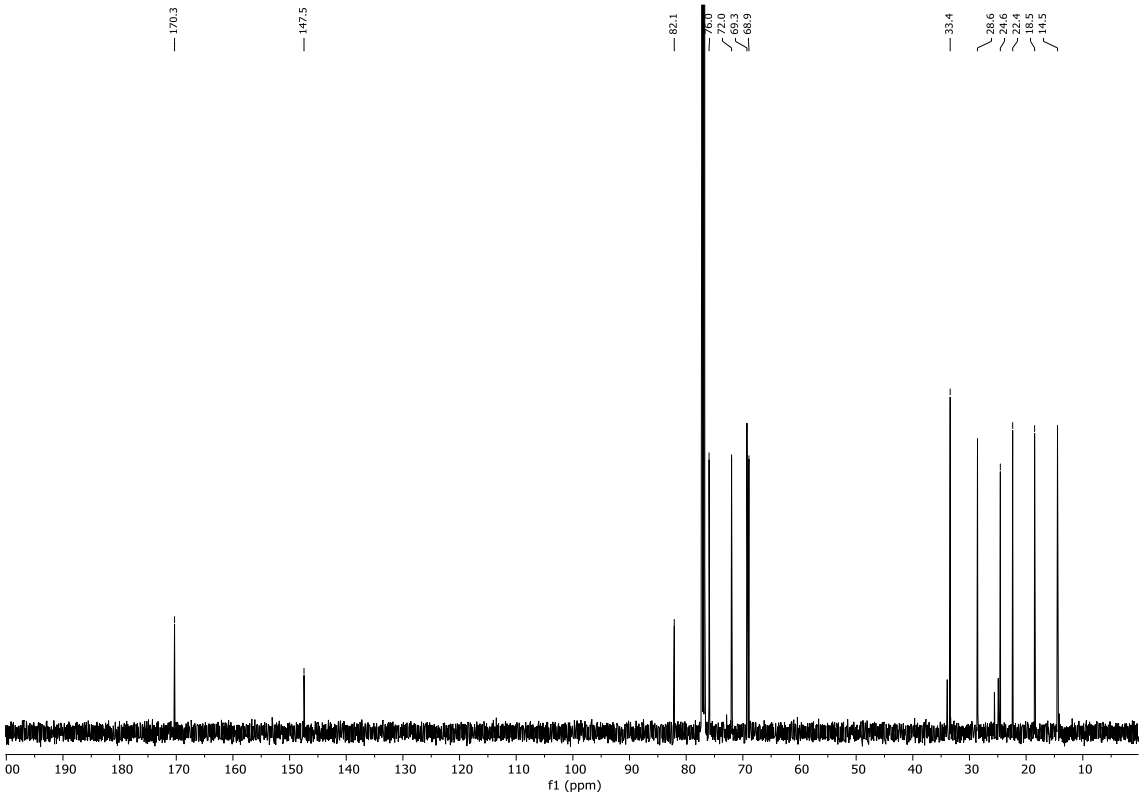


Figure S28: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **7**

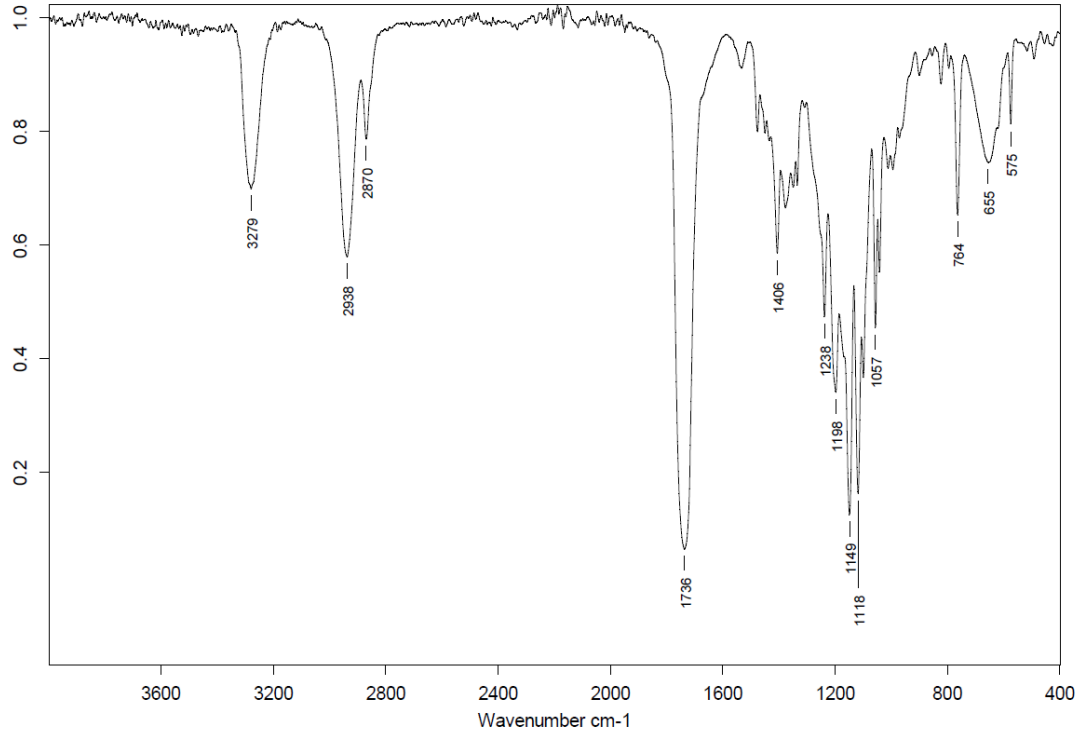


Figure S29: IR spectrum (neat) of **7**

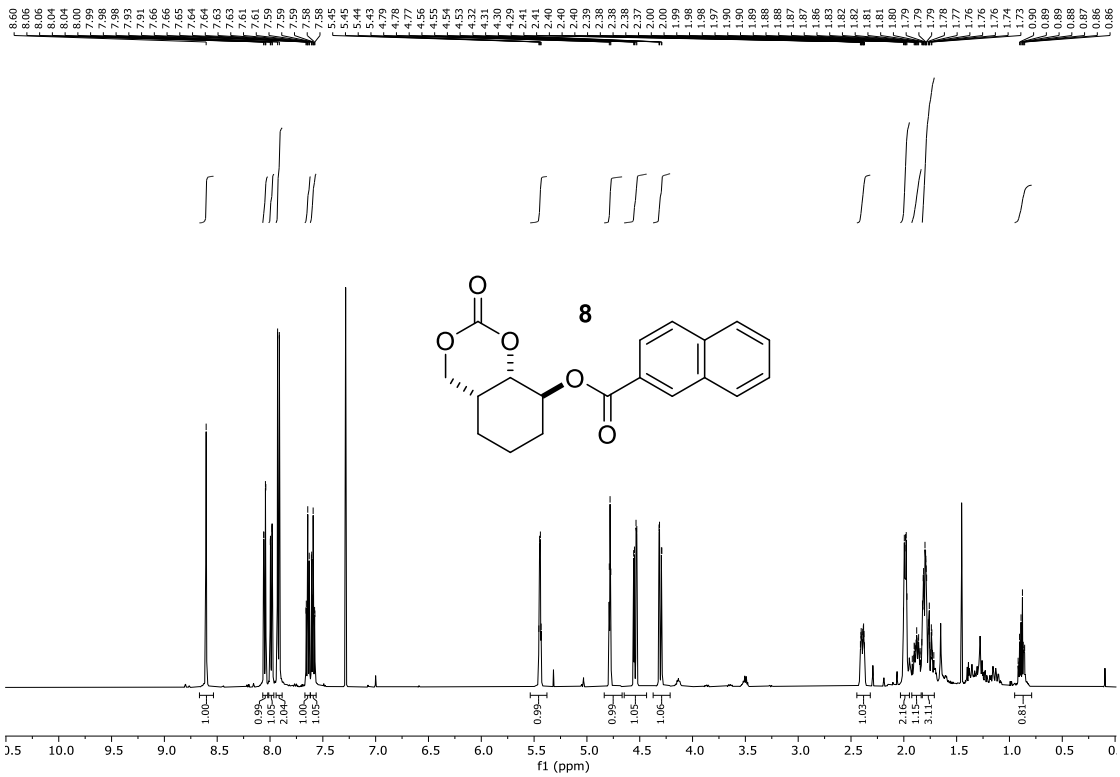


Figure S30: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **8**

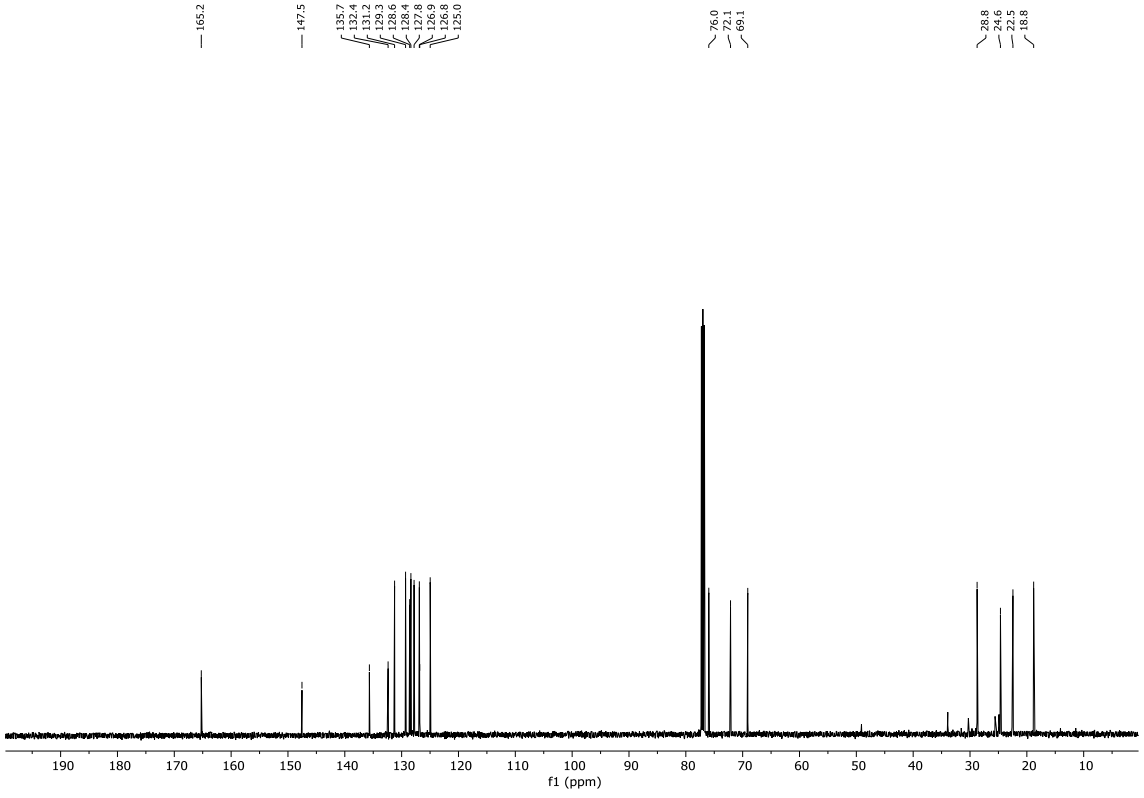


Figure S31:**^{13}C NMR** ($CDCl_3$, 126 MHz) of **8**

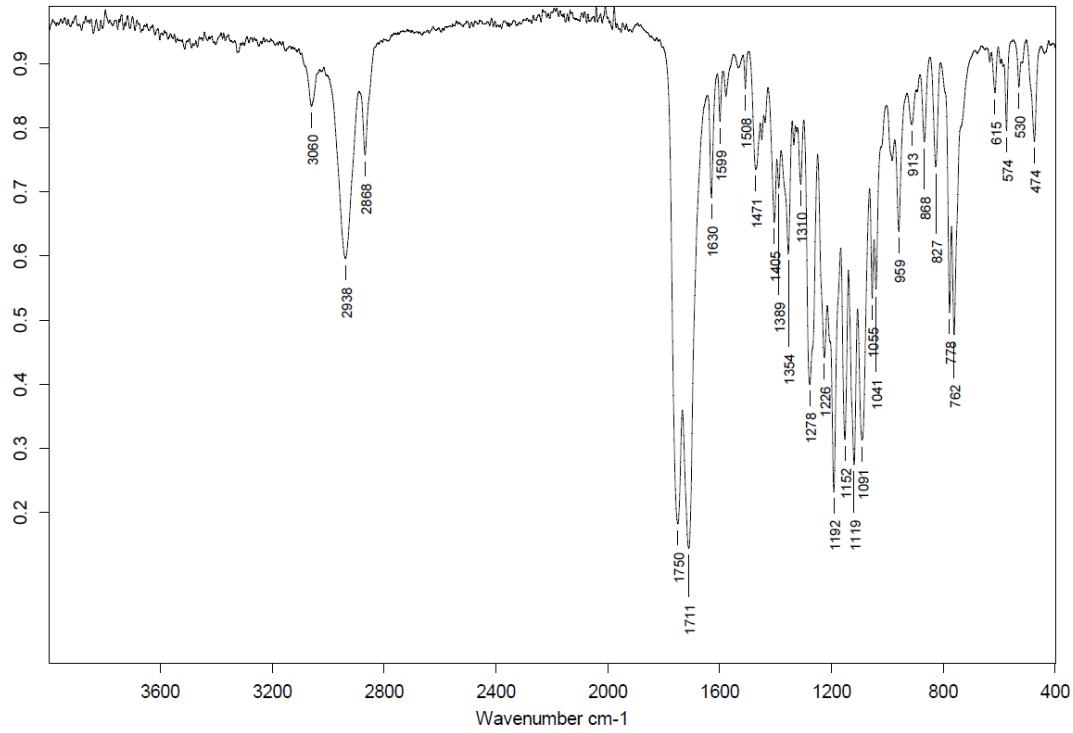


Figure S32: IR spectrum (neat) of **8**

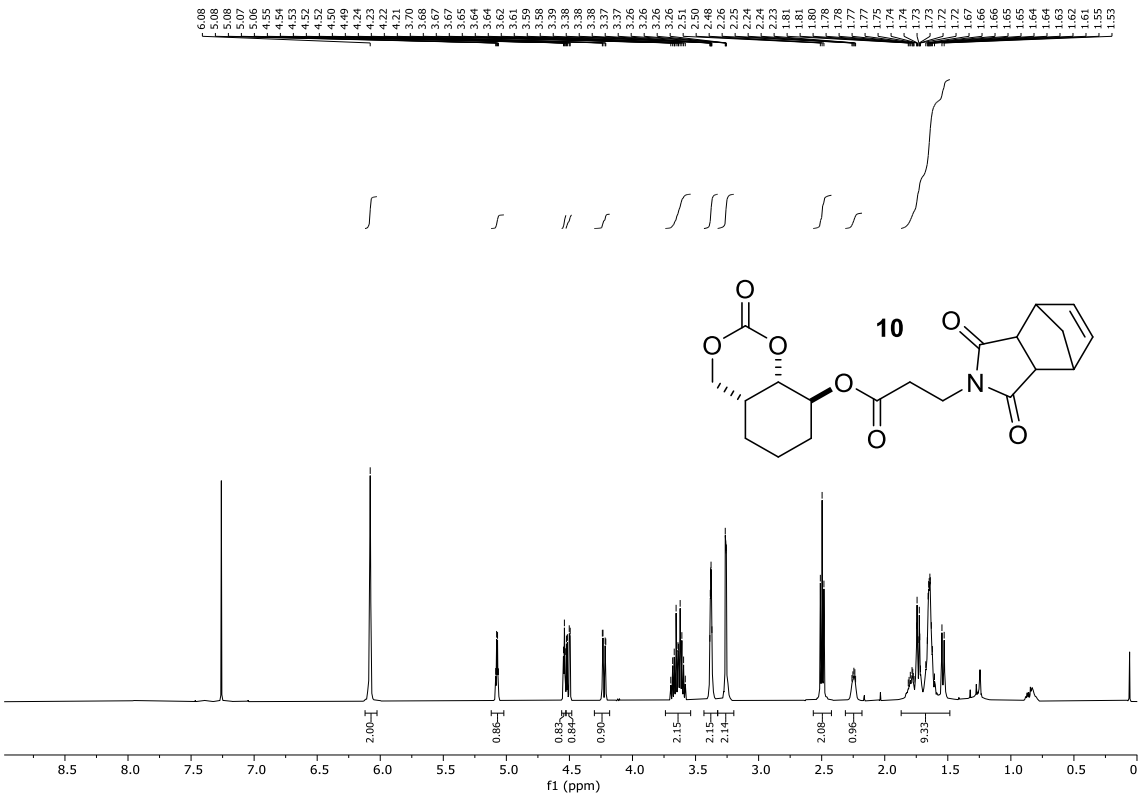


Figure S33: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **10**

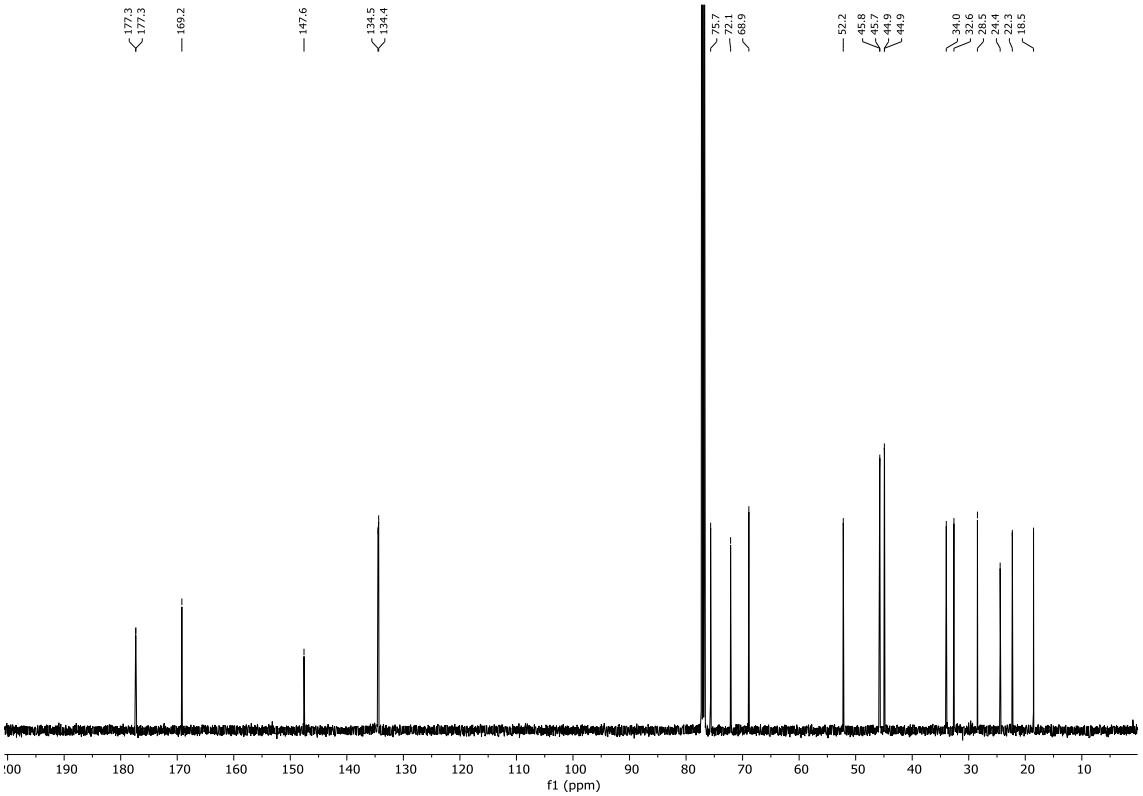


Figure S34:**^{13}C NMR** ($CDCl_3$, 126 MHz) of **10**

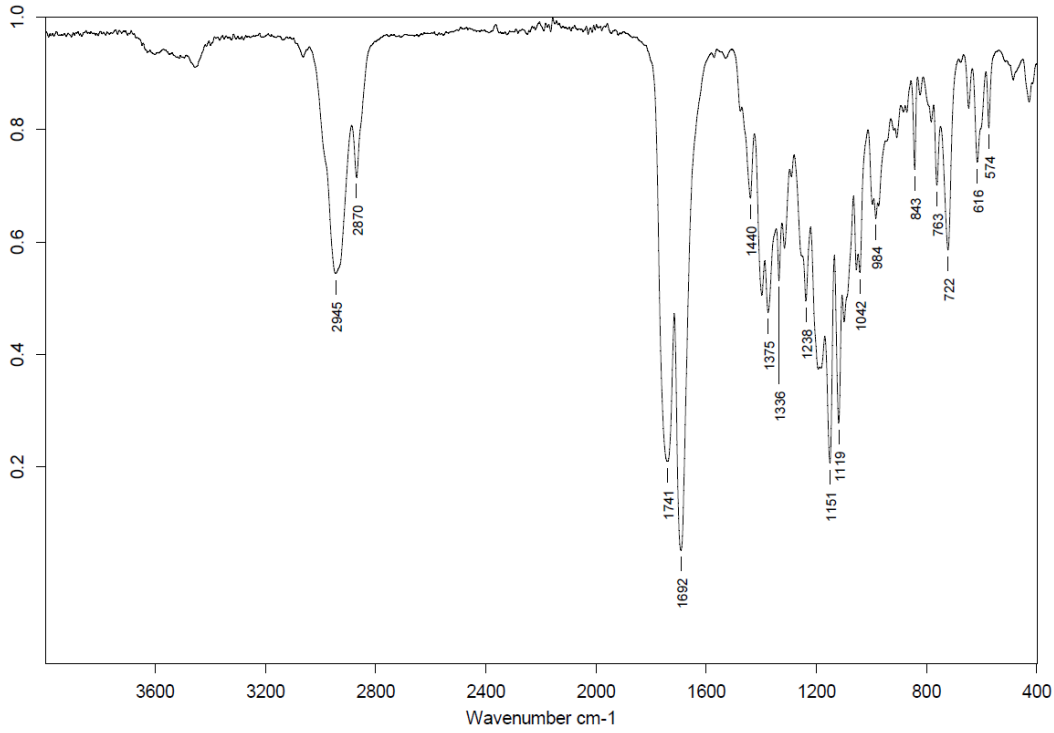


Figure S35: IR spectrum (neat) of **10**

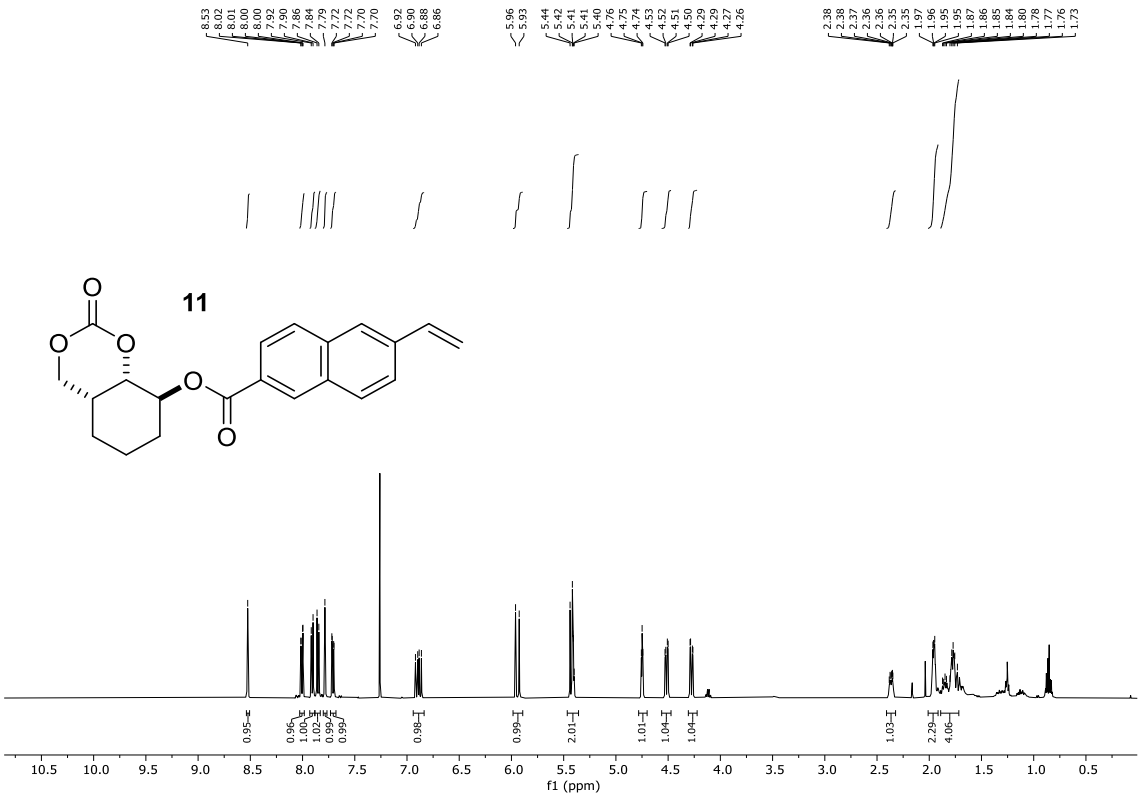


Figure S36: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **11**

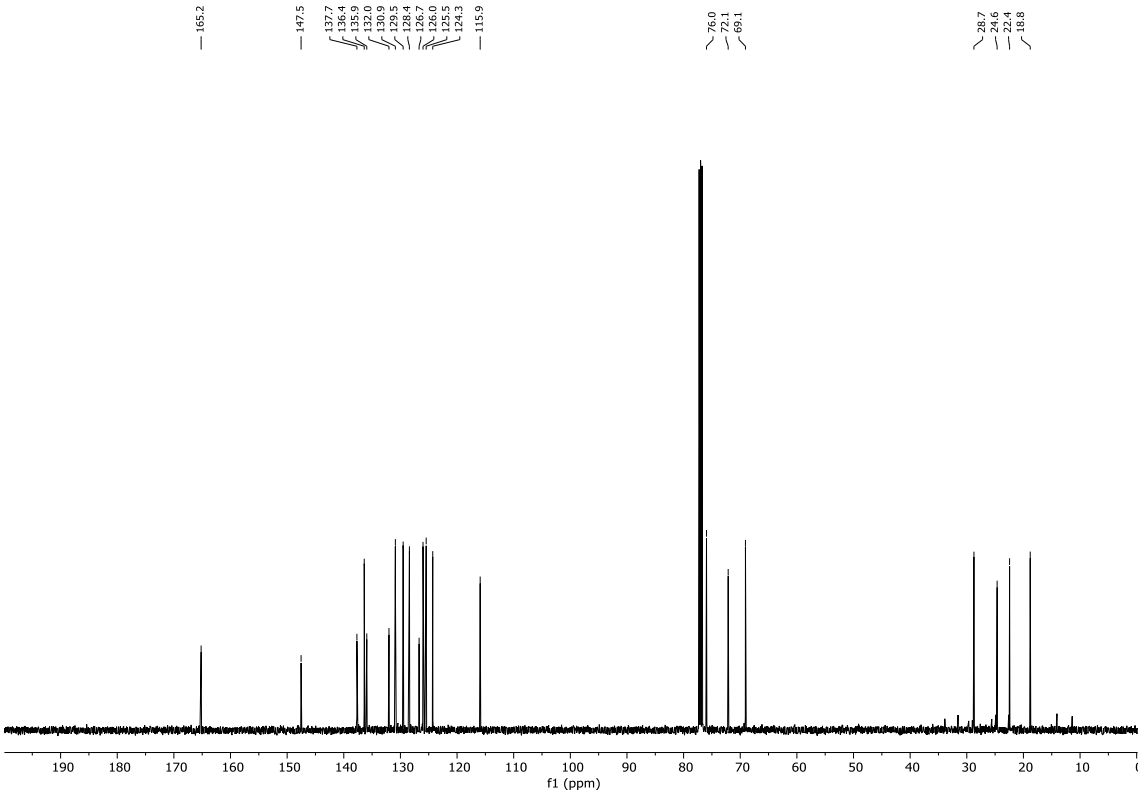


Figure S37: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **11**

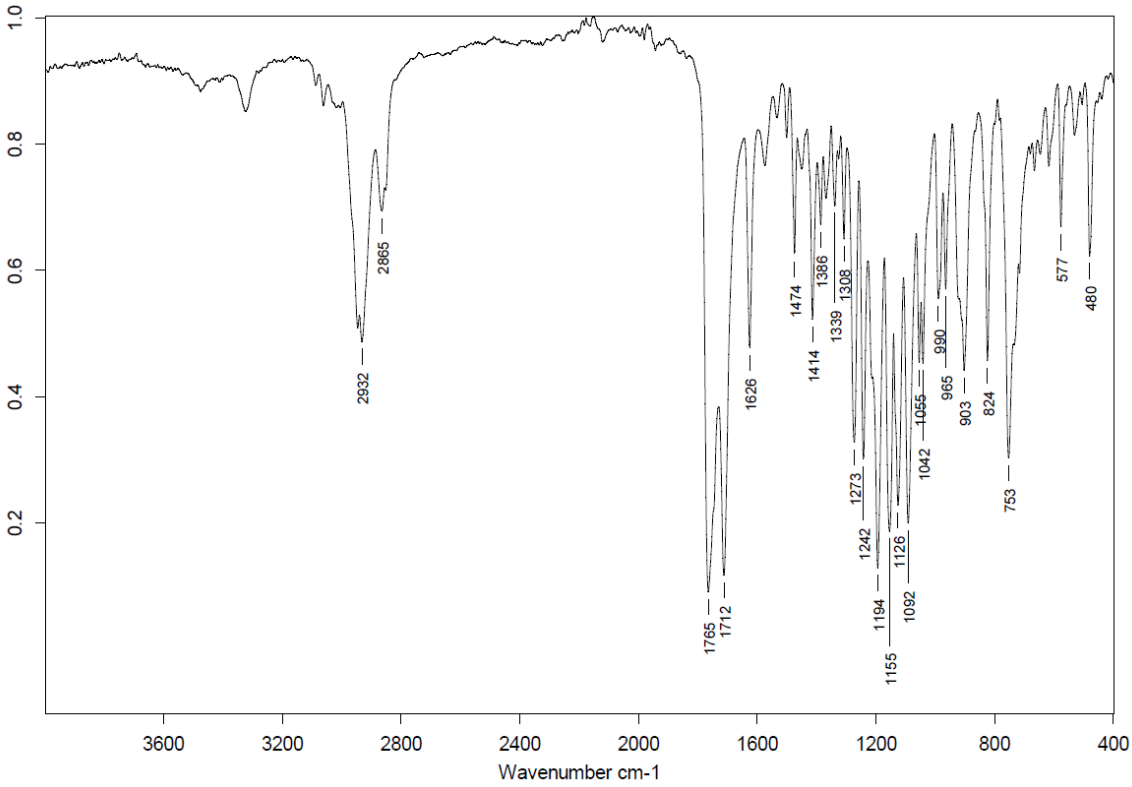


Figure S38: IR spectrum (neat) of **11**

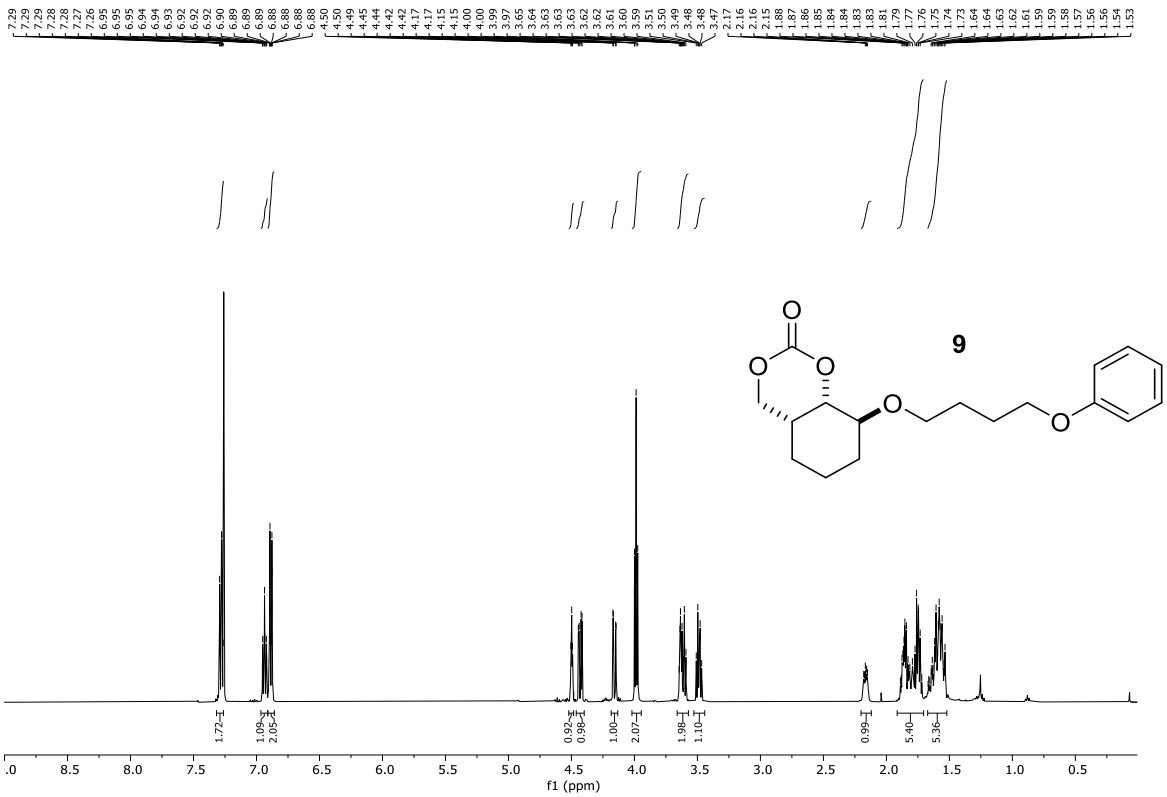


Figure S39: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **9**

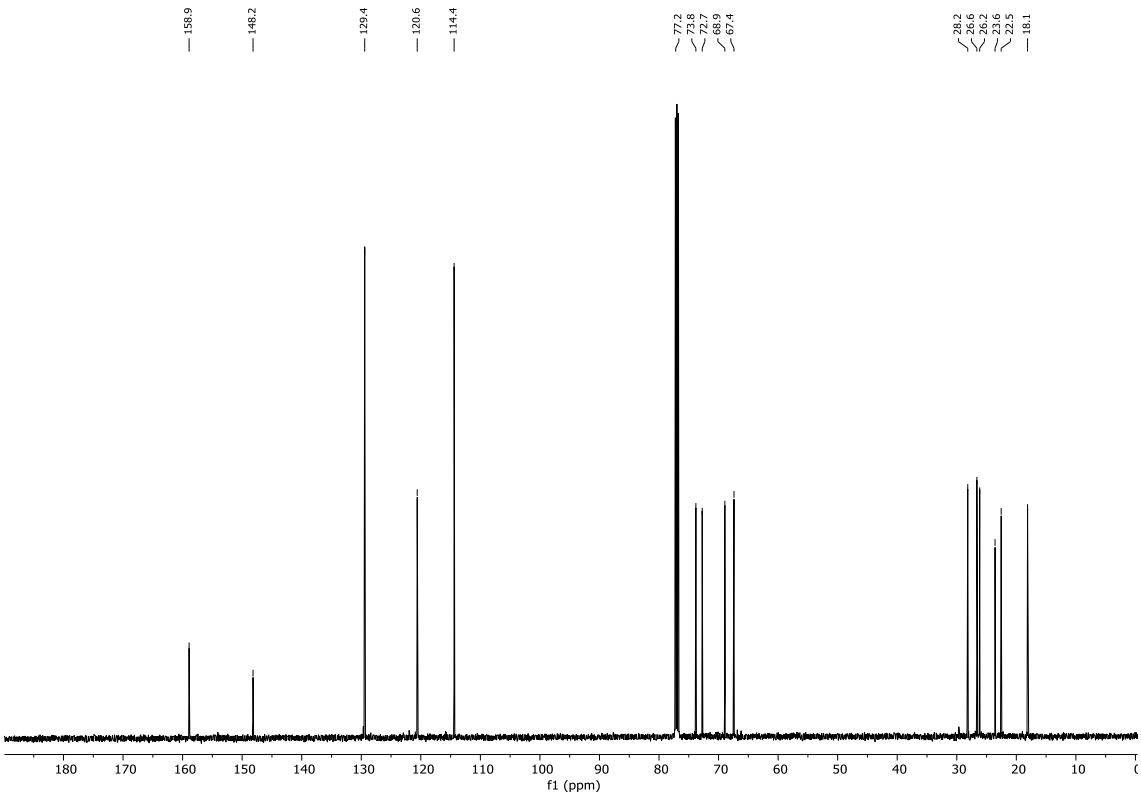


Figure S40: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **9**

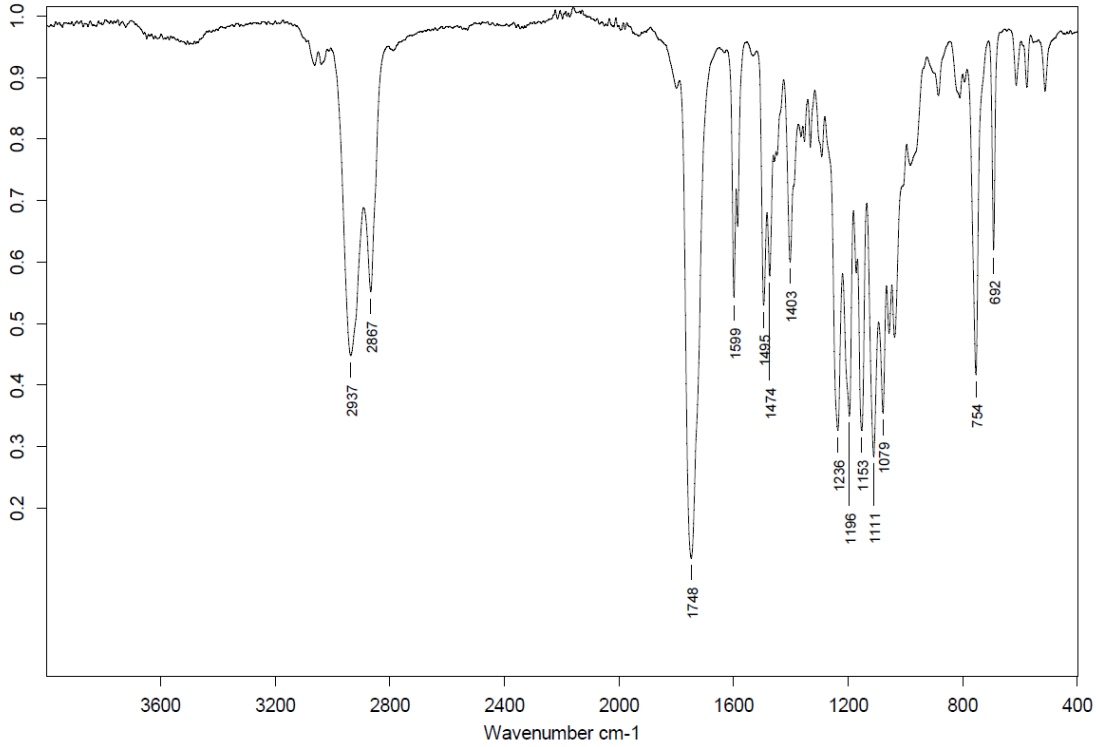


Figure S41: IR spectrum (neat) of **9**

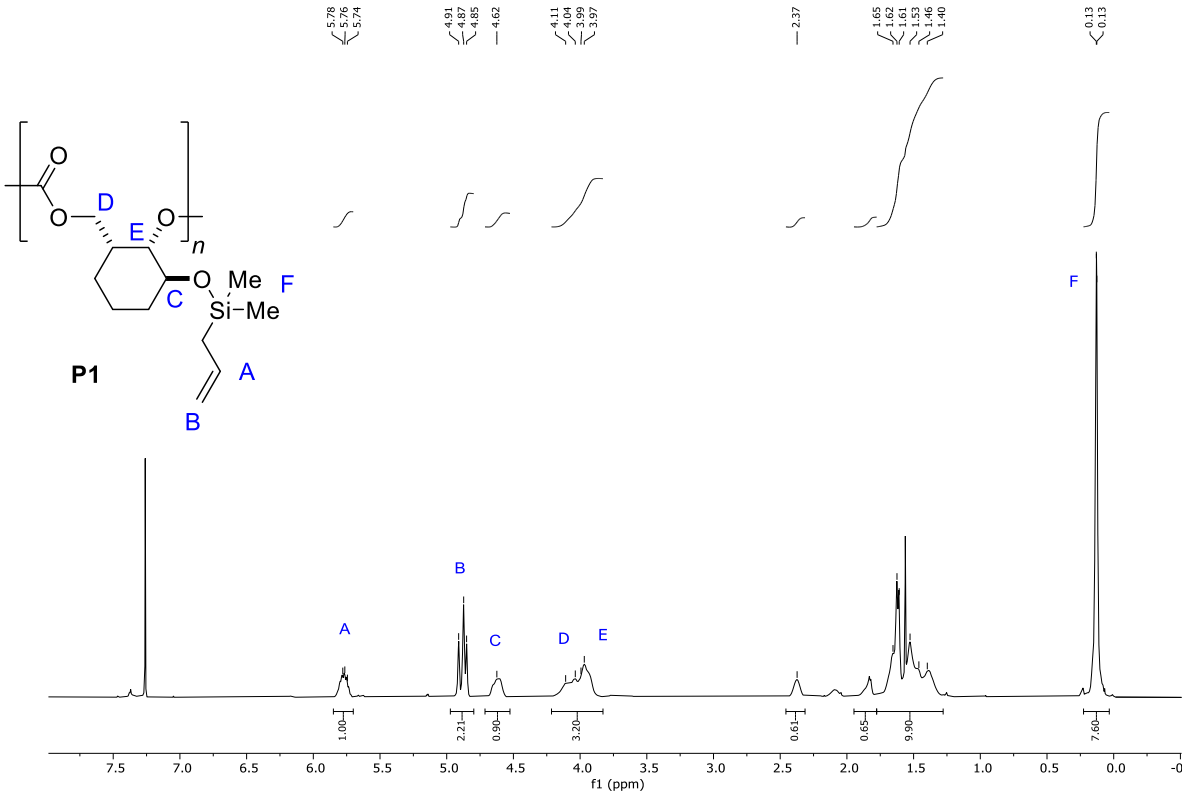


Figure S42: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P1**

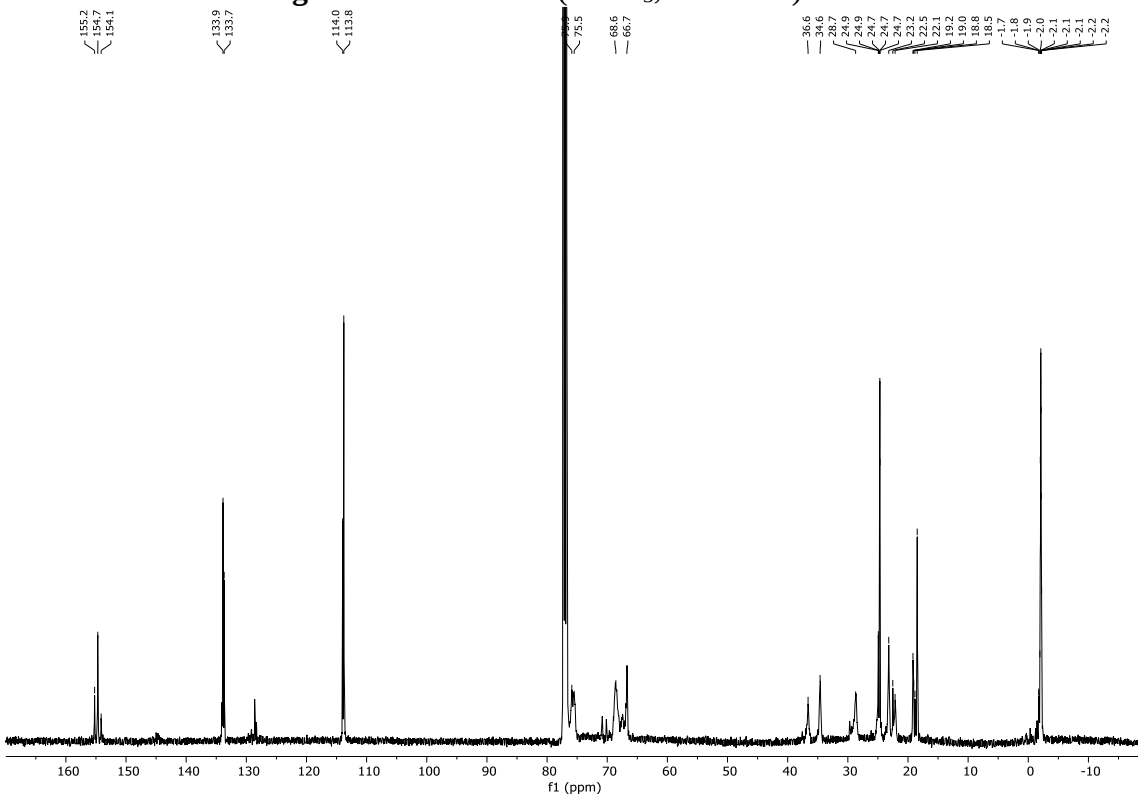


Figure S43:**^{13}C NMR** ($CDCl_3$, 126 MHz) of **P1**

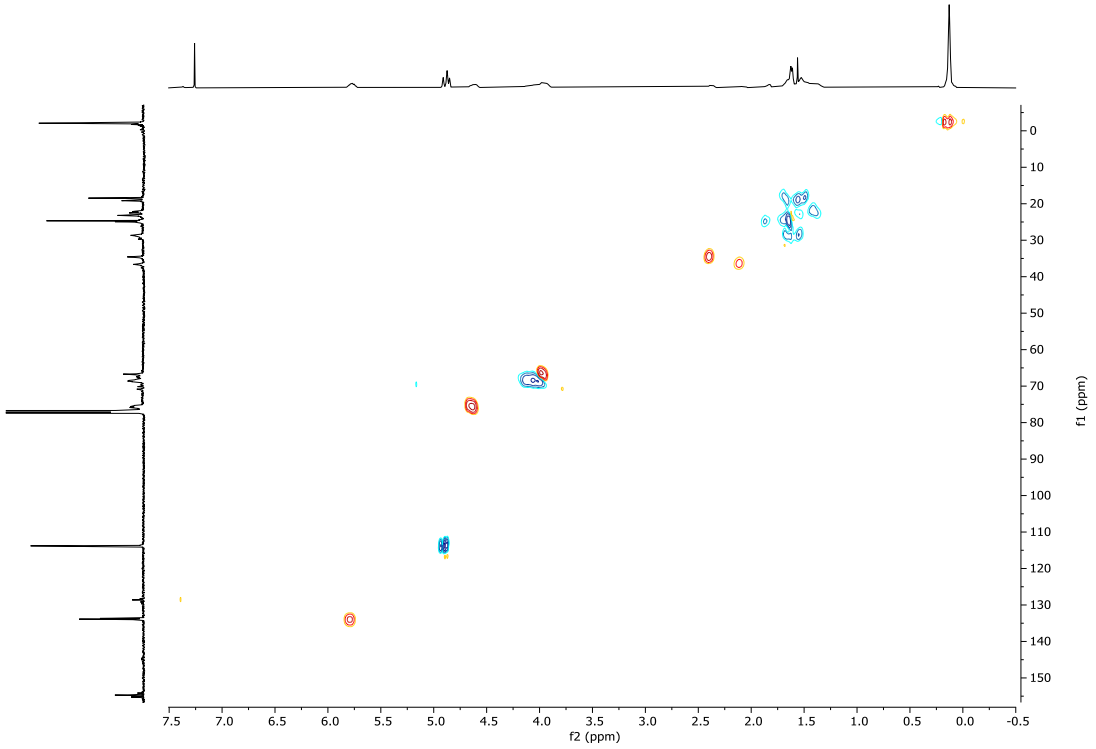


Figure S44: **^{1}H - ^{13}C HSQC** (500 MHz, $CDCl_3$) of **P1**

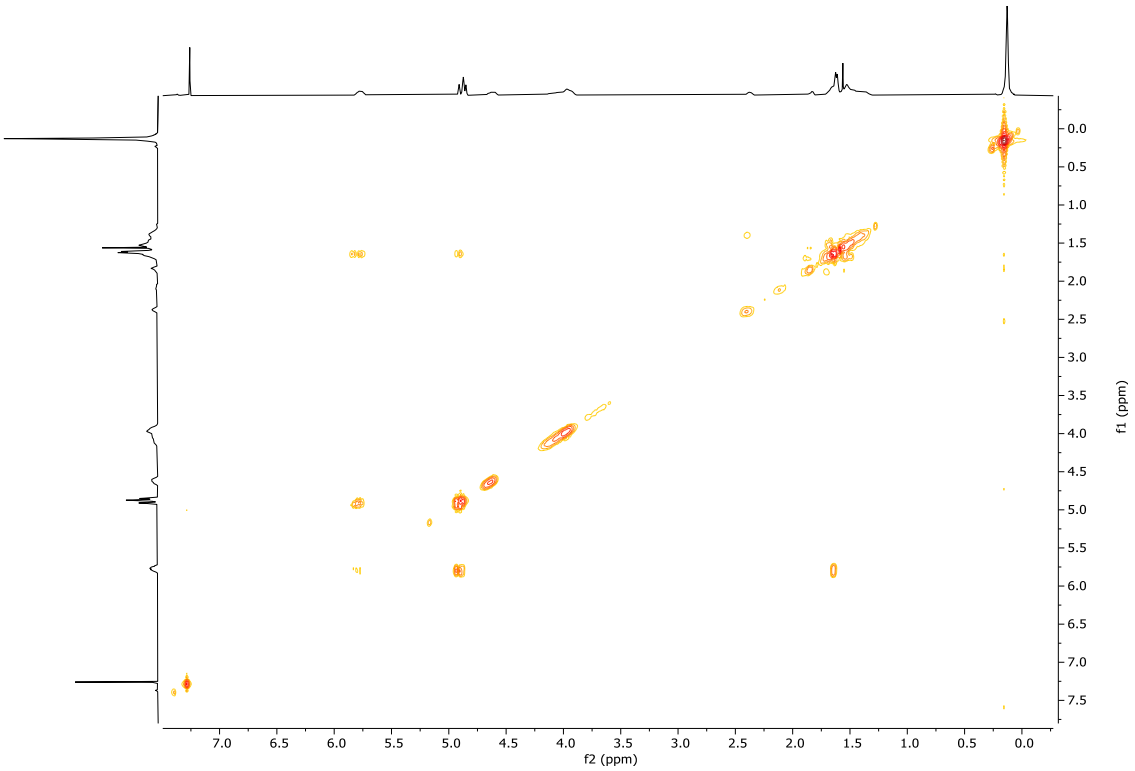


Figure S45: **^{1}H-^{1}H COSY** (500 MHz, $CDCl_3$) of **P1**

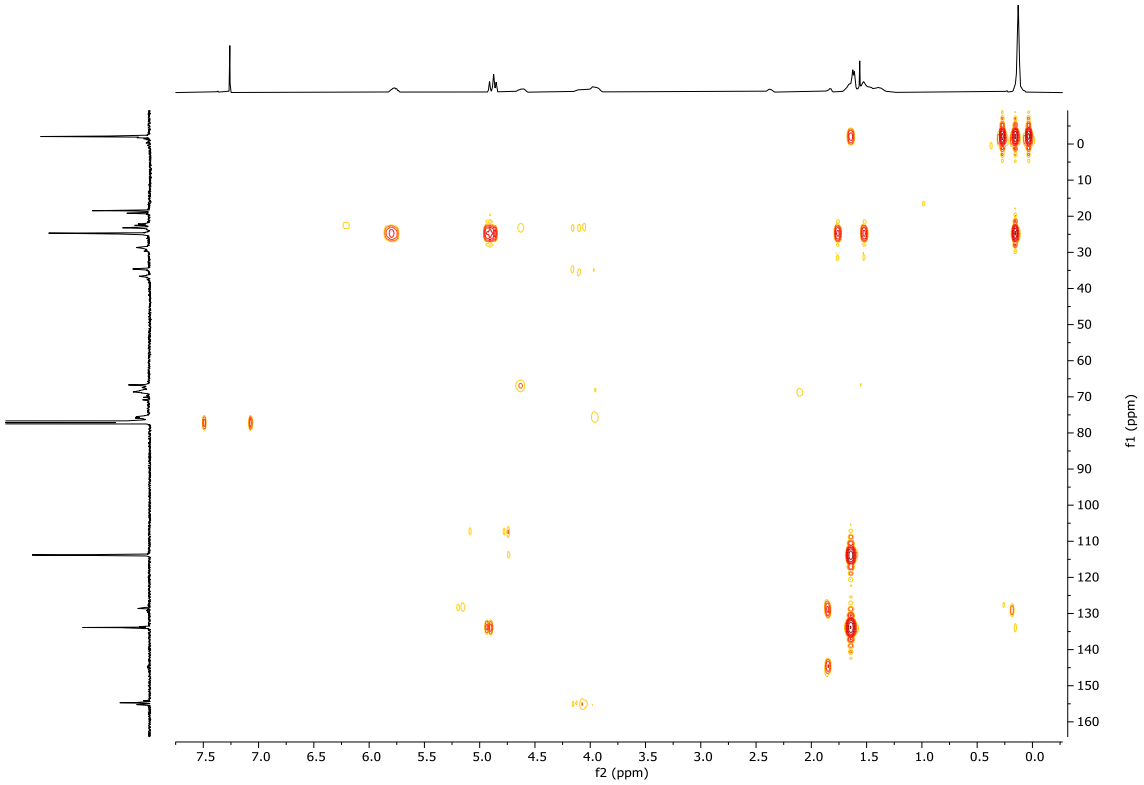


Figure S46: **^{1}H-^{13}C HMBC** ($CDCl_3$, 500 MHz) of **P1**

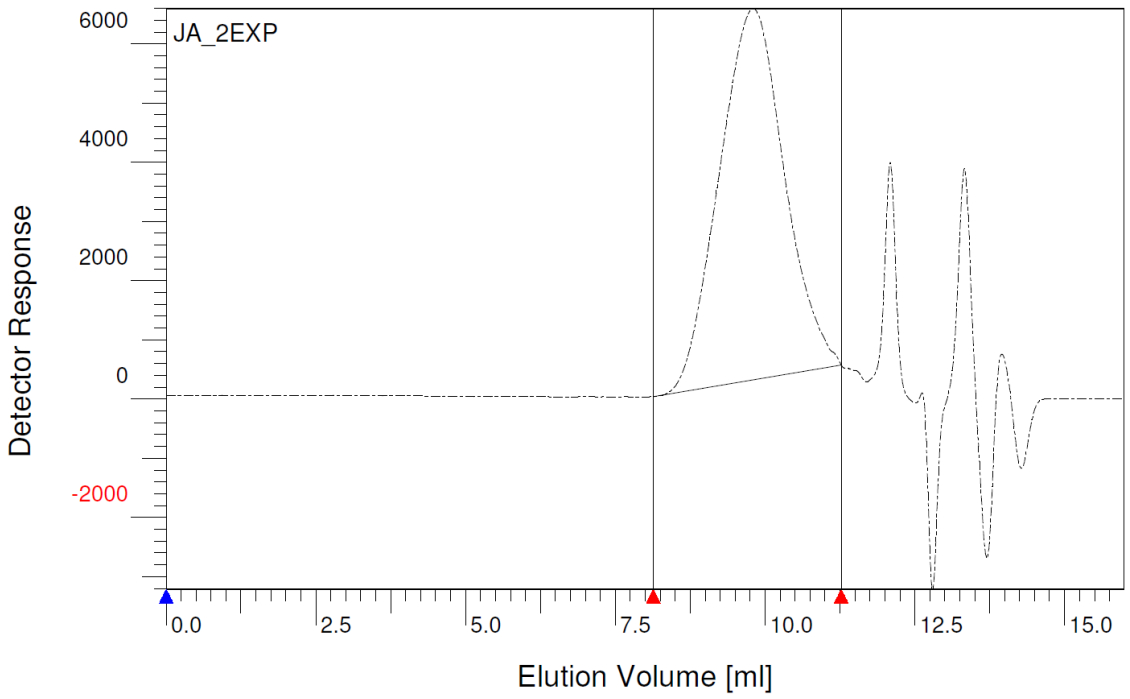


Figure S47: **GPC** analysis of **P1**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
5.5582e3	8.5911e3	1.2818e4	6.7719e3	1.5457

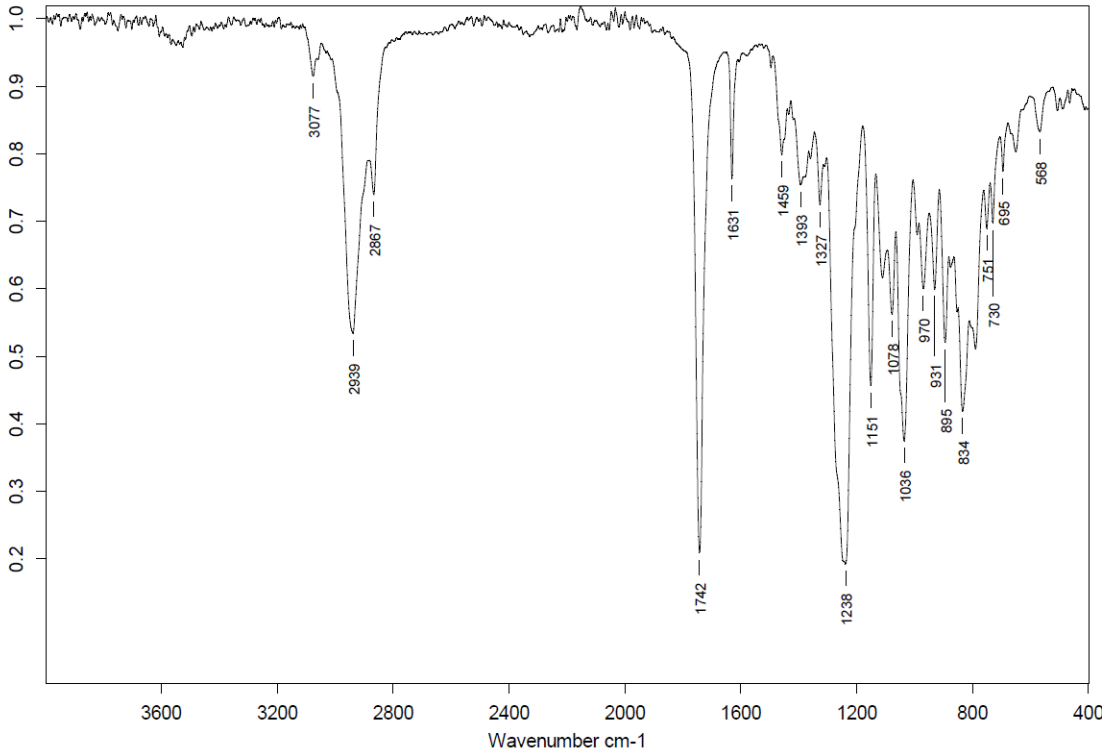


Figure S48: IR spectrum (neat) of **P1**

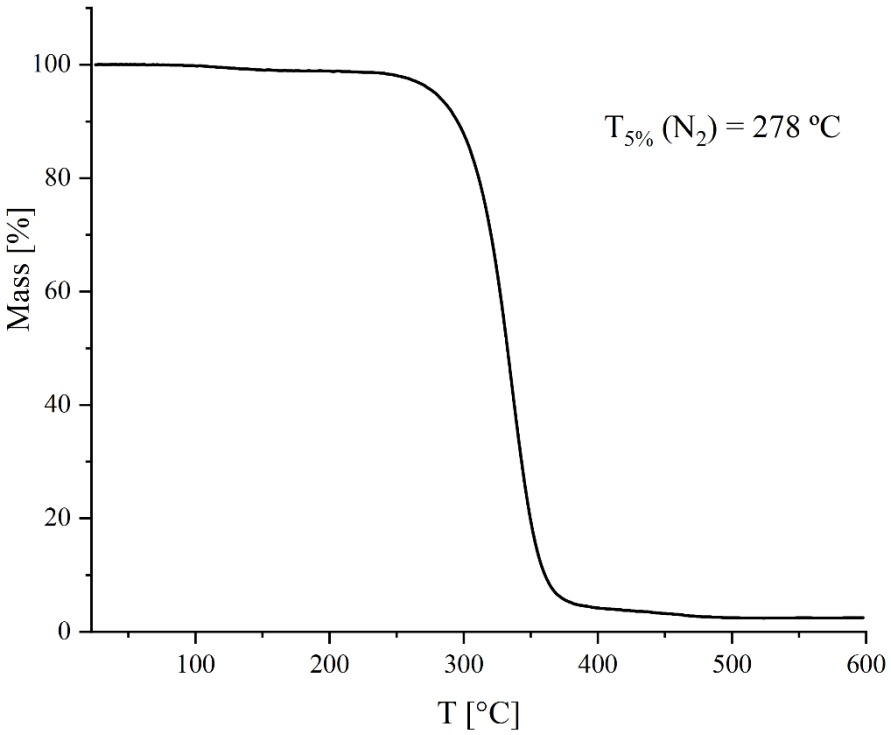


Figure S49: **TGA** thermogram of **P1**

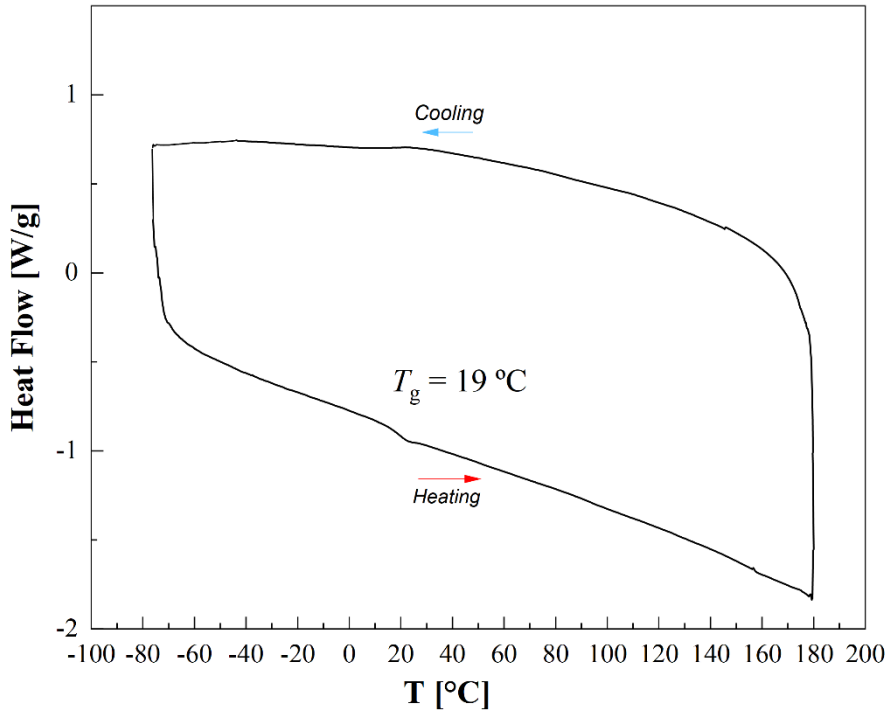


Figure S50: **DSC** thermogram of **P1**

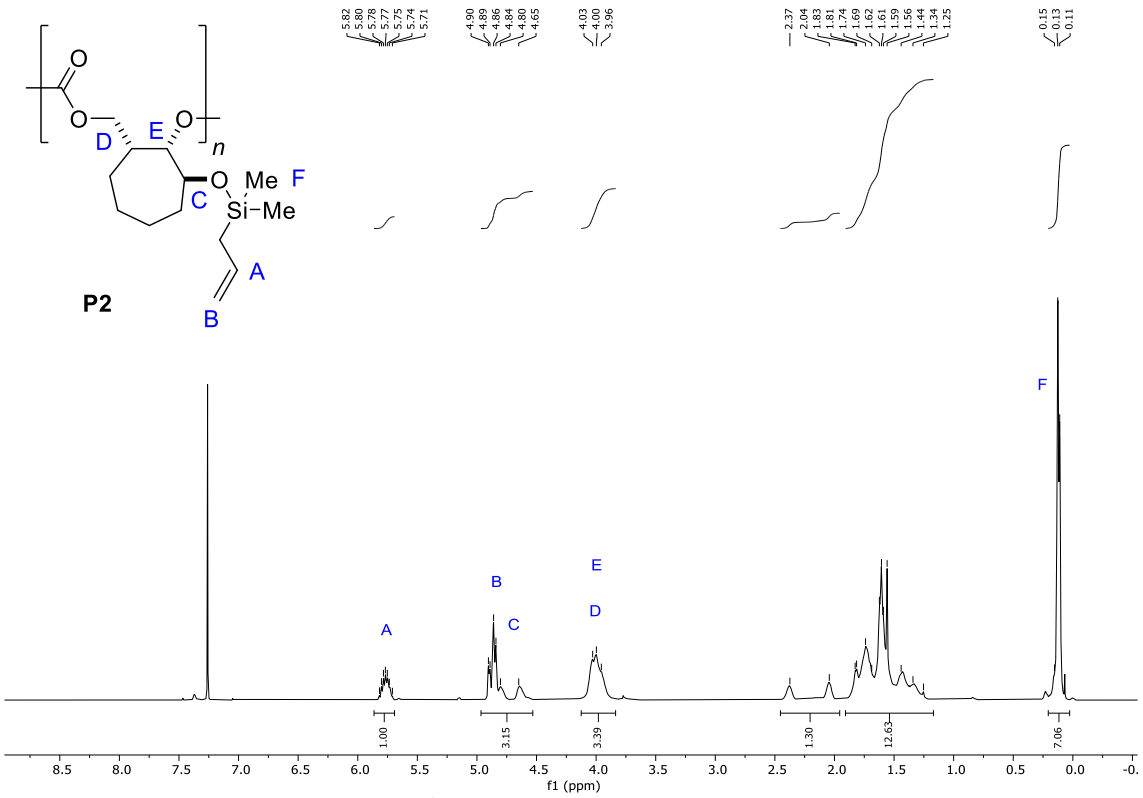


Figure S51: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P2**

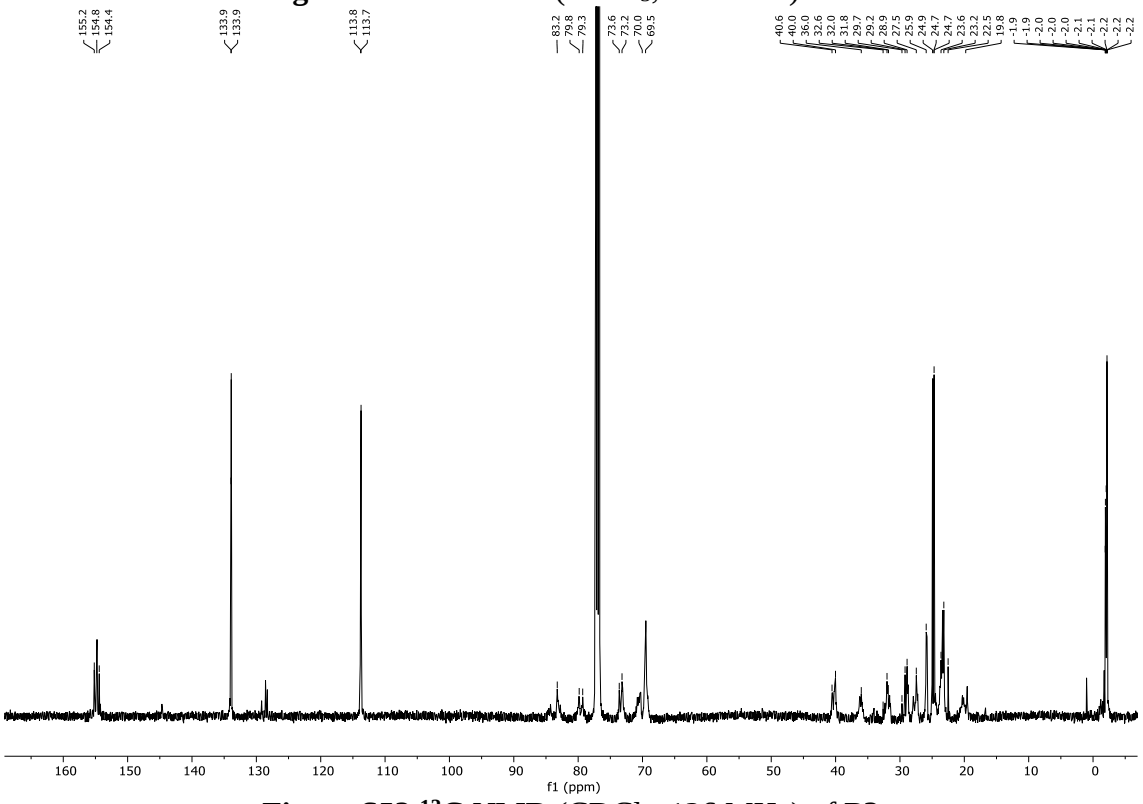


Figure S52:**^{13}C NMR** ($CDCl_3$, 126 MHz) of **P2**

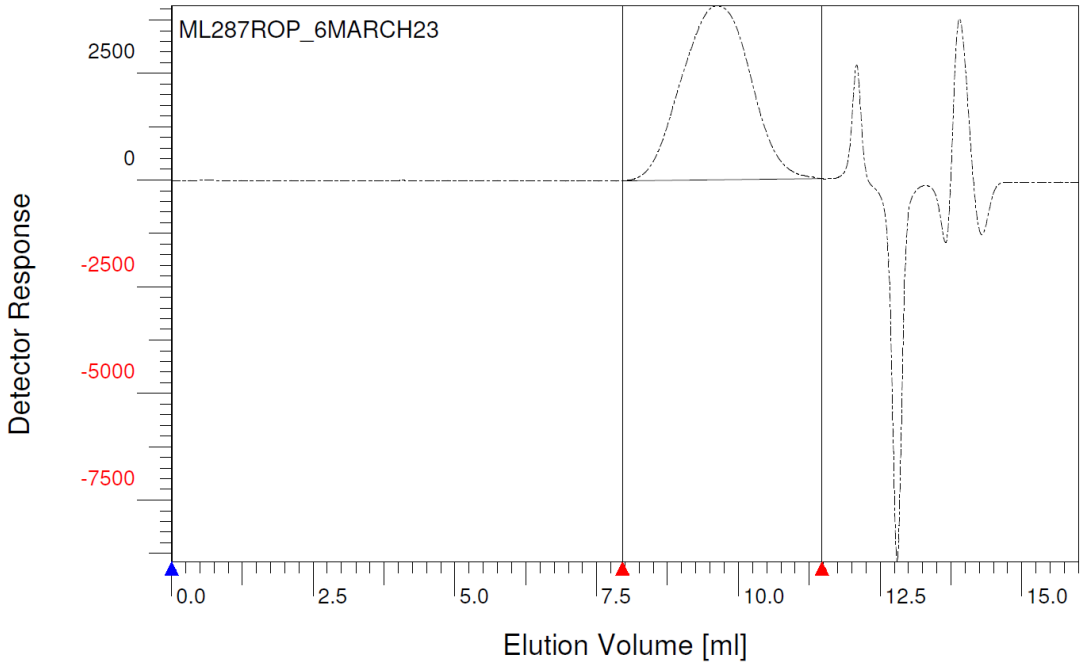


Figure S53: GPC analysis of **P2**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
6.8256e3	1.1227e3	1.7790e4	8.5218e3	1.6449

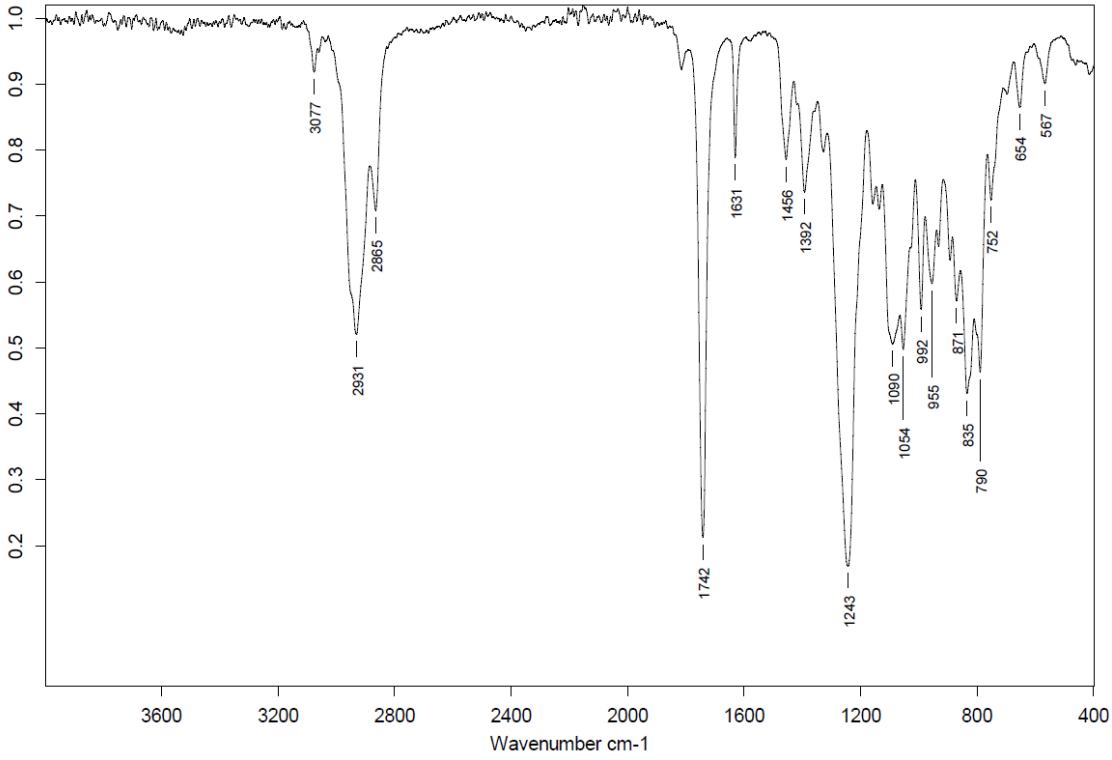


Figure S54: IR spectrum (neat) of **P2**

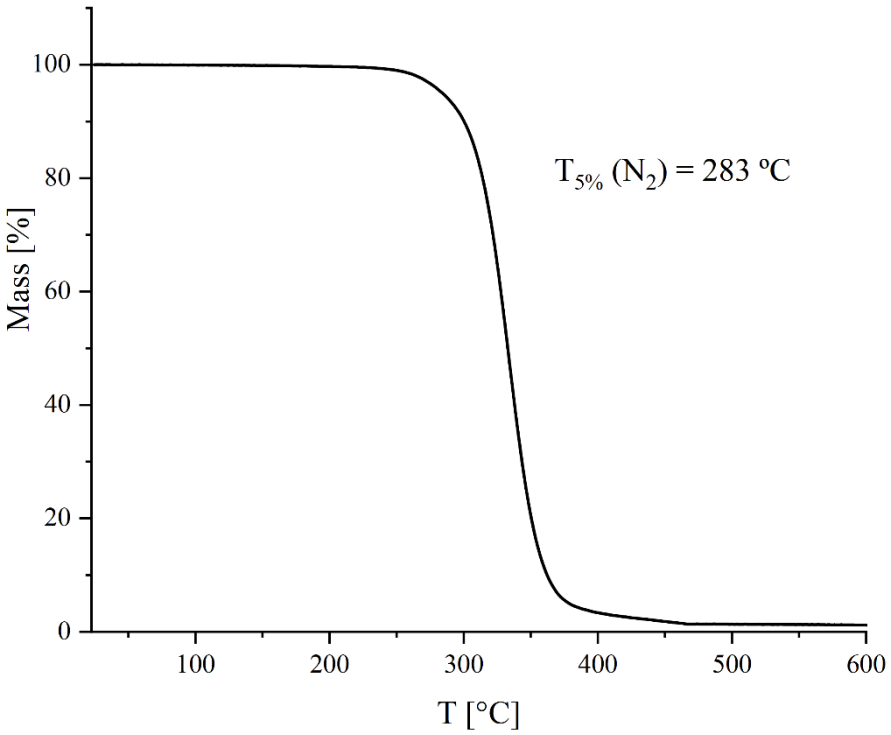


Figure S55: TGA thermogram of **P2**

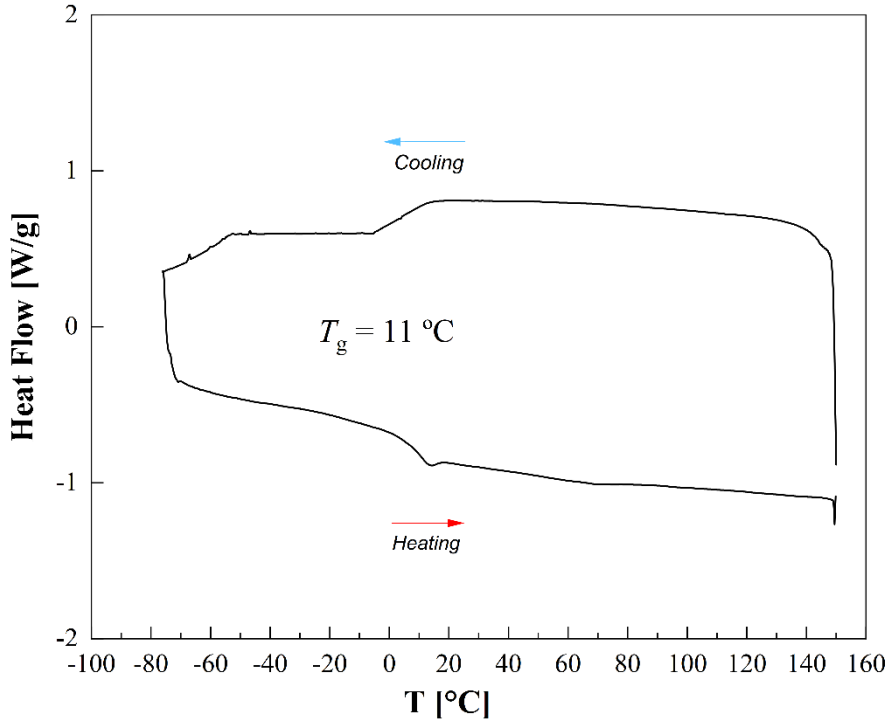


Figure S56: DSC thermogram of **P2**

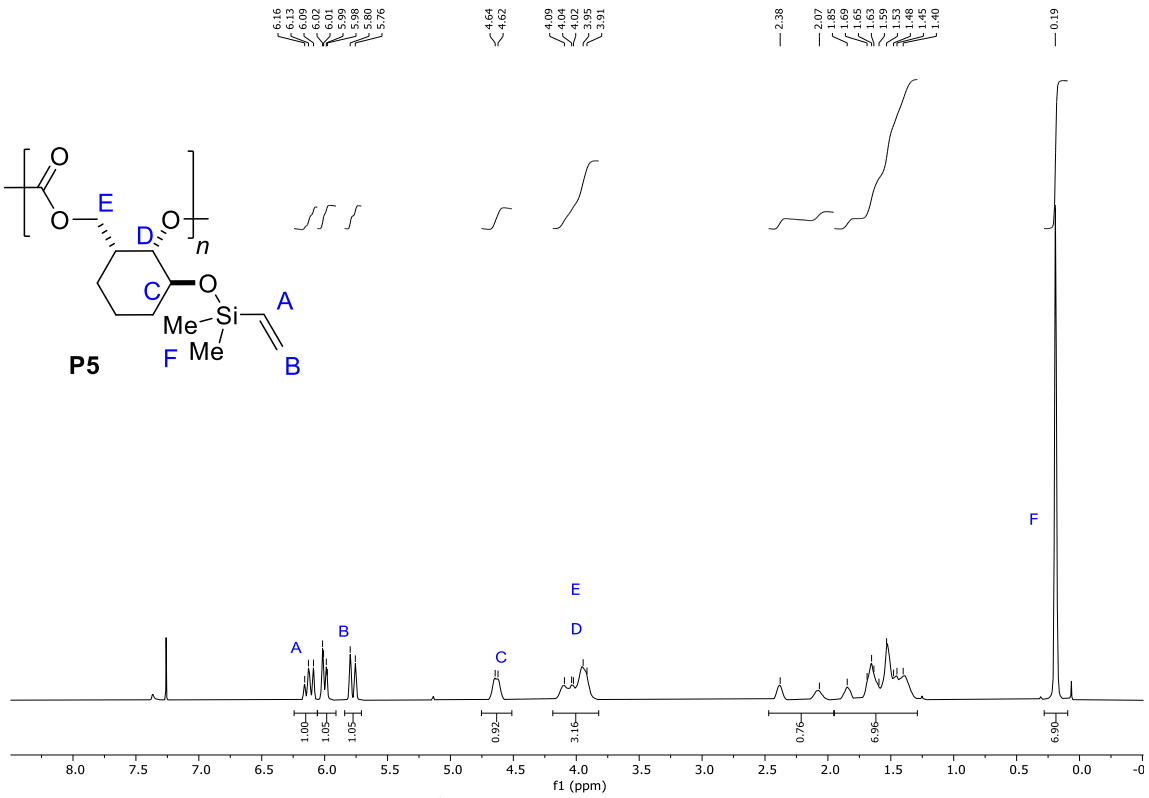


Figure S57: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P5**

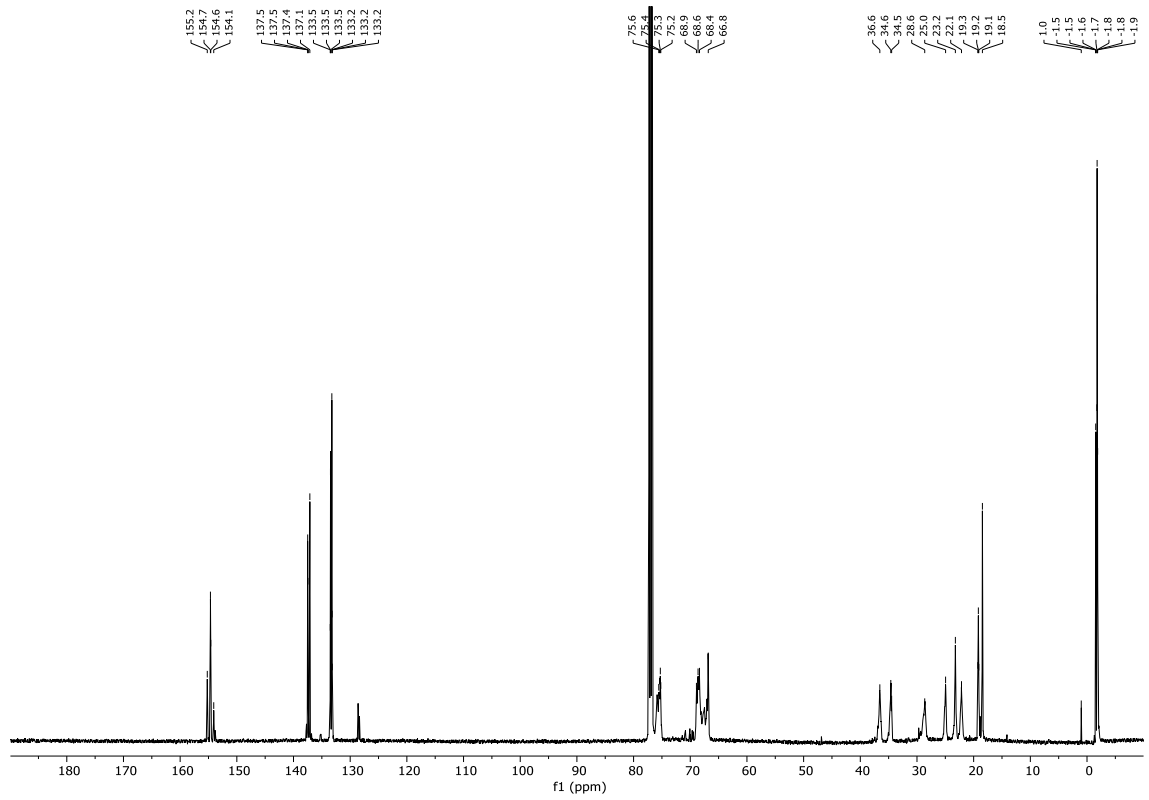


Figure S58: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P5**

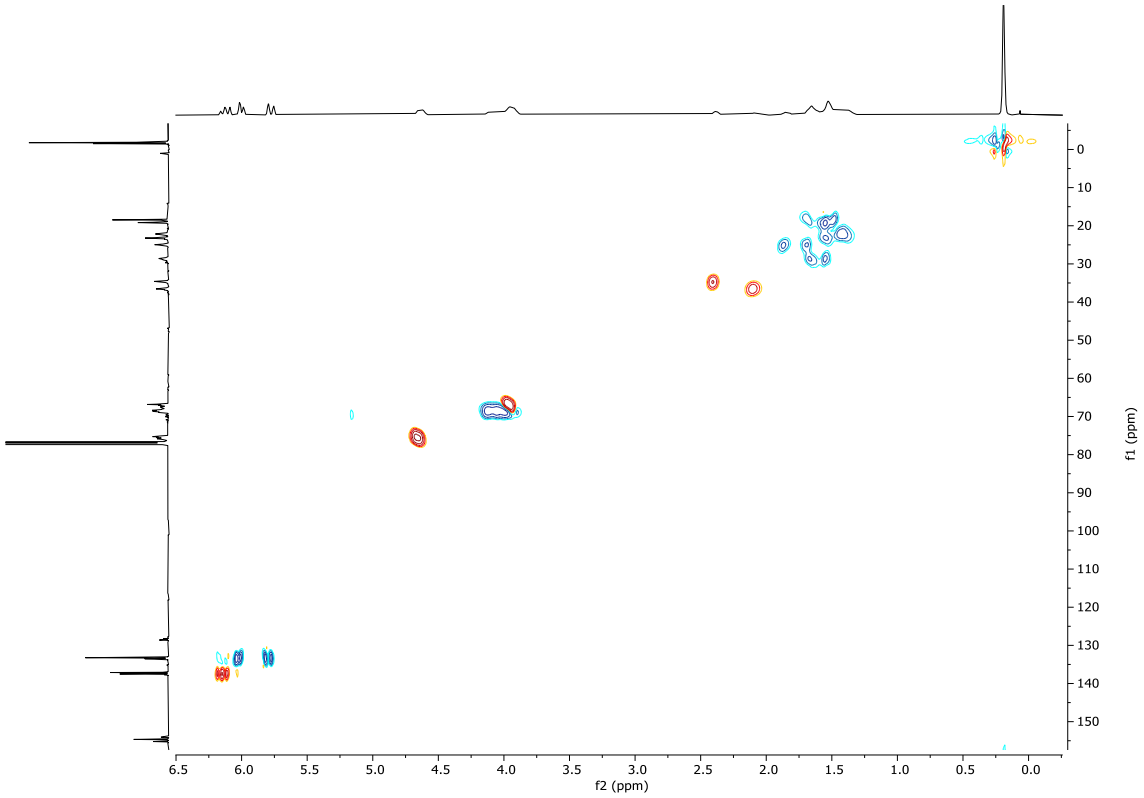


Figure S59*:* **^{1}H - ^{13}C HSQC** (500 MHz, $CDCl_3$) of **P5**

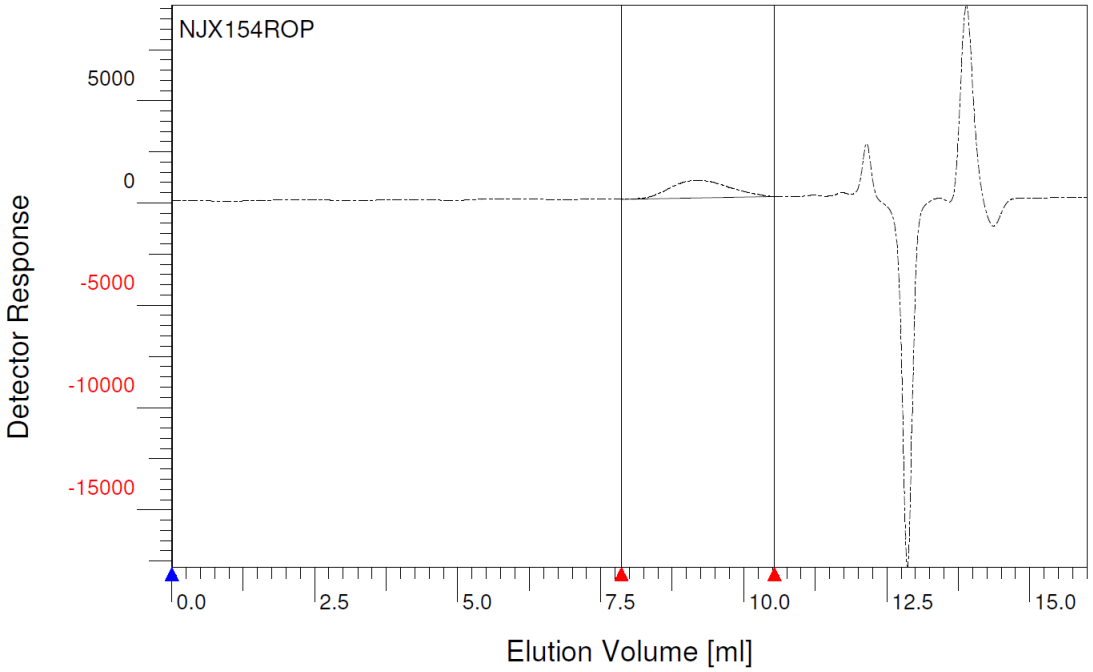


Figure S60: GPC analysis of **P5**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
1.1708e4	1.6922e4	2.3233e4	1.5913e4	1.4453

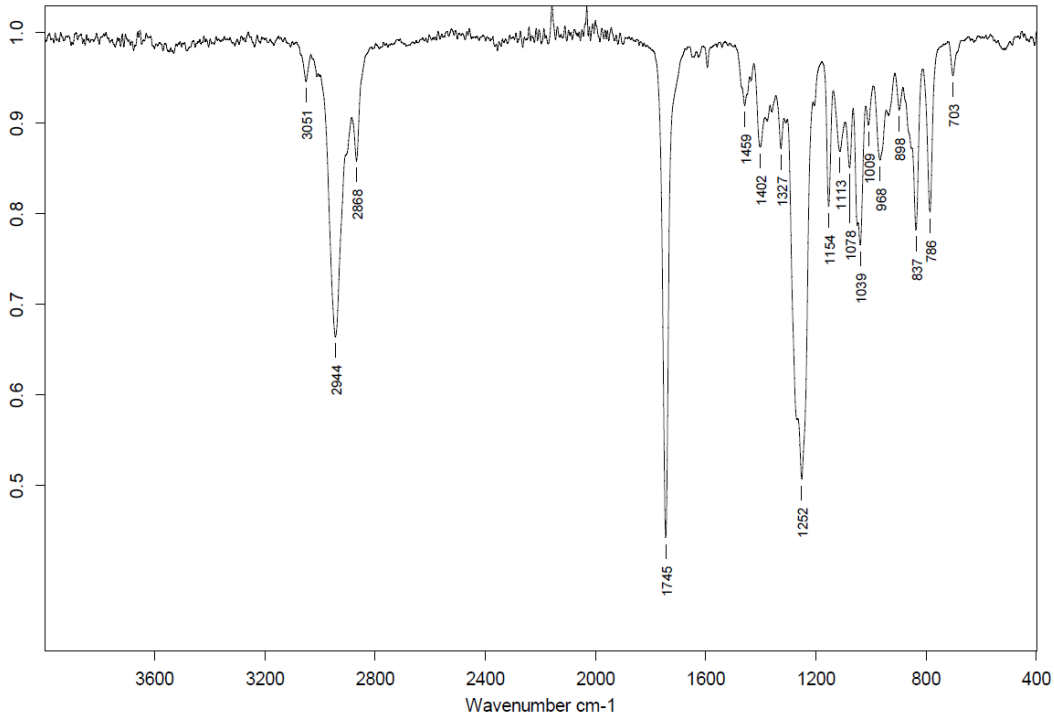


Figure S61: IR spectrum (neat) of **P5**

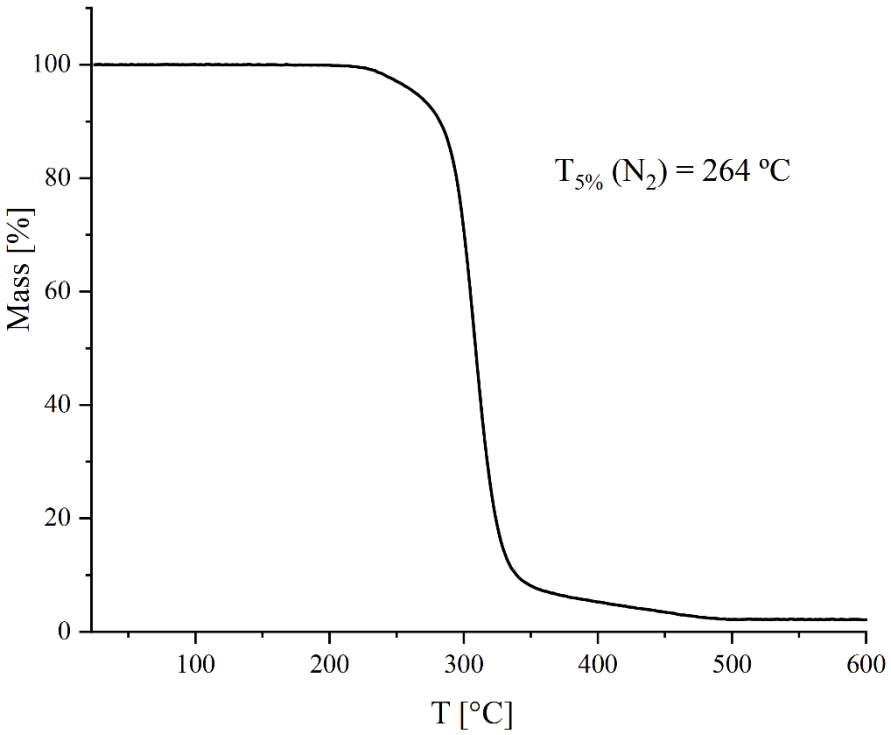


Figure S62: TGA thermogram of **P5**

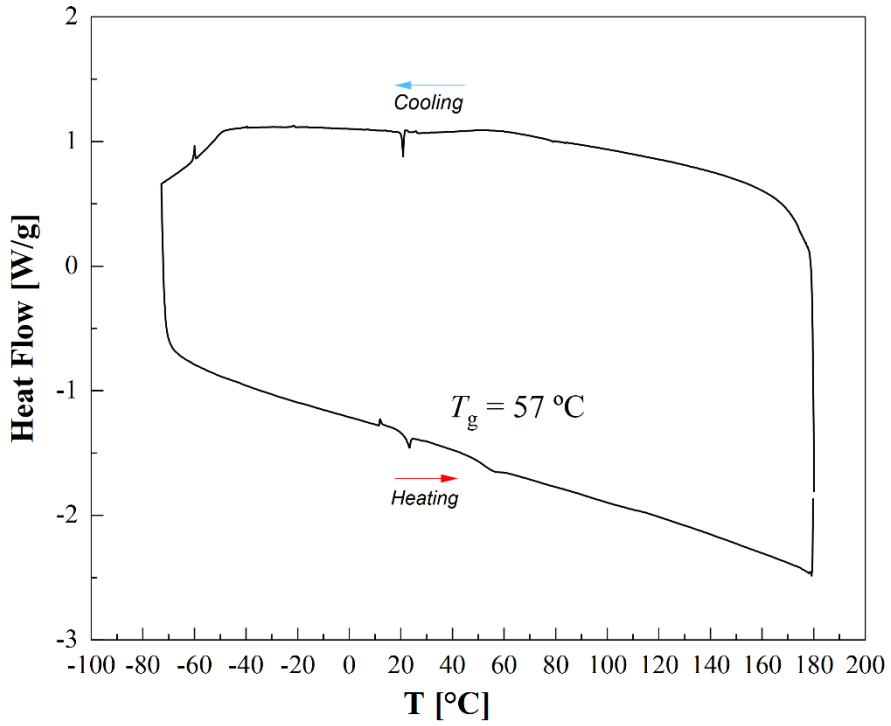


Figure S63: DSC thermogram of **P5**

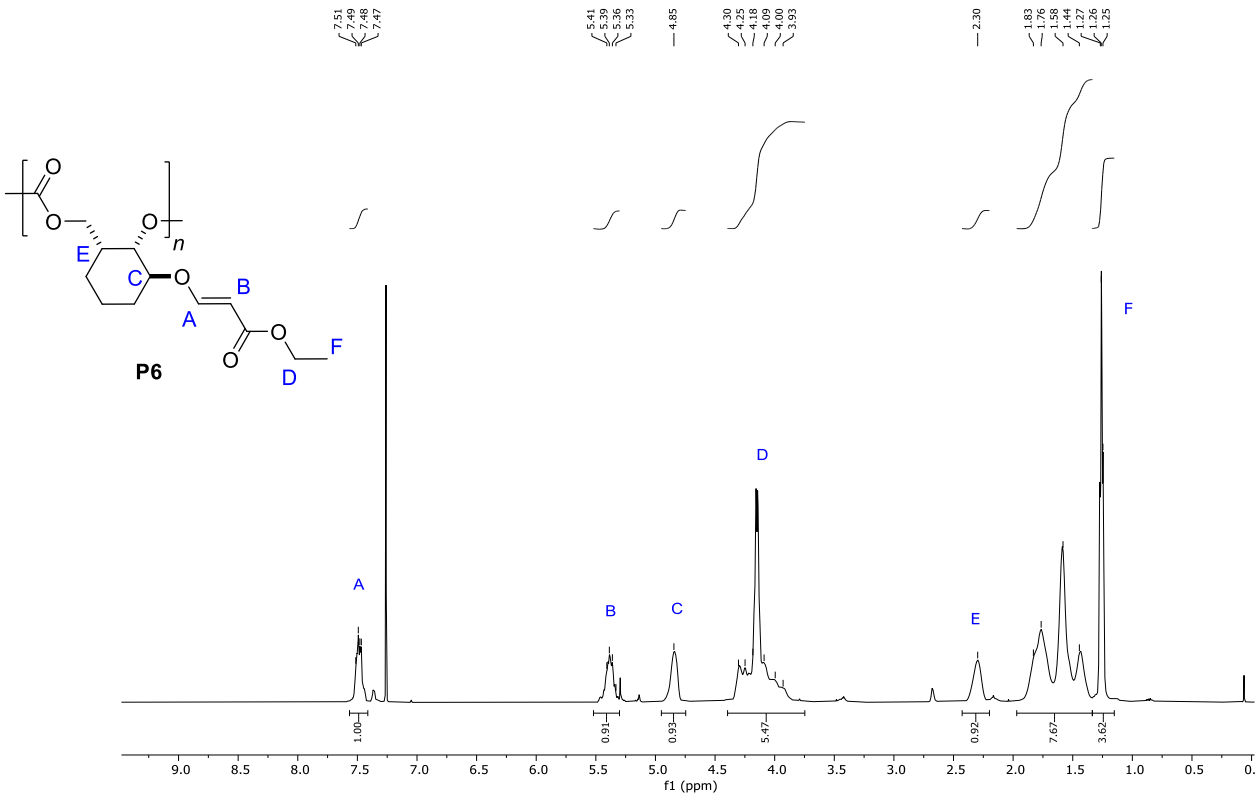


Figure S64*:* **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P6**

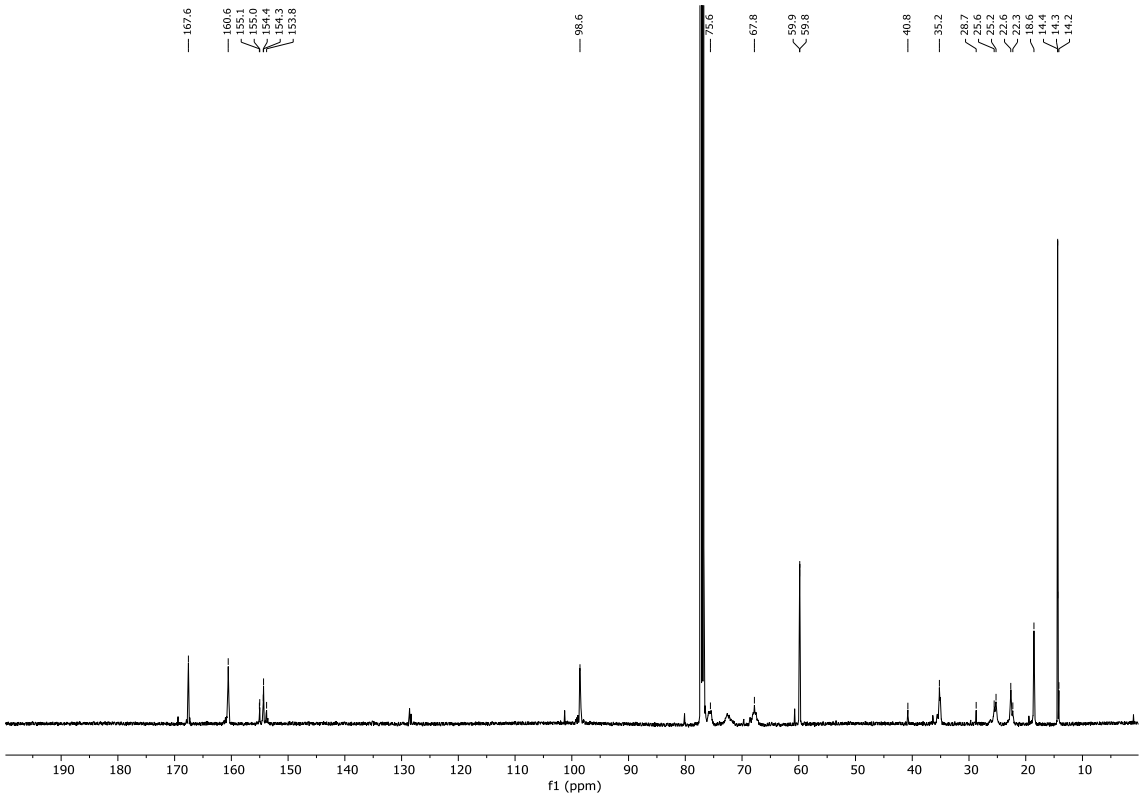


Figure S65: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P6**

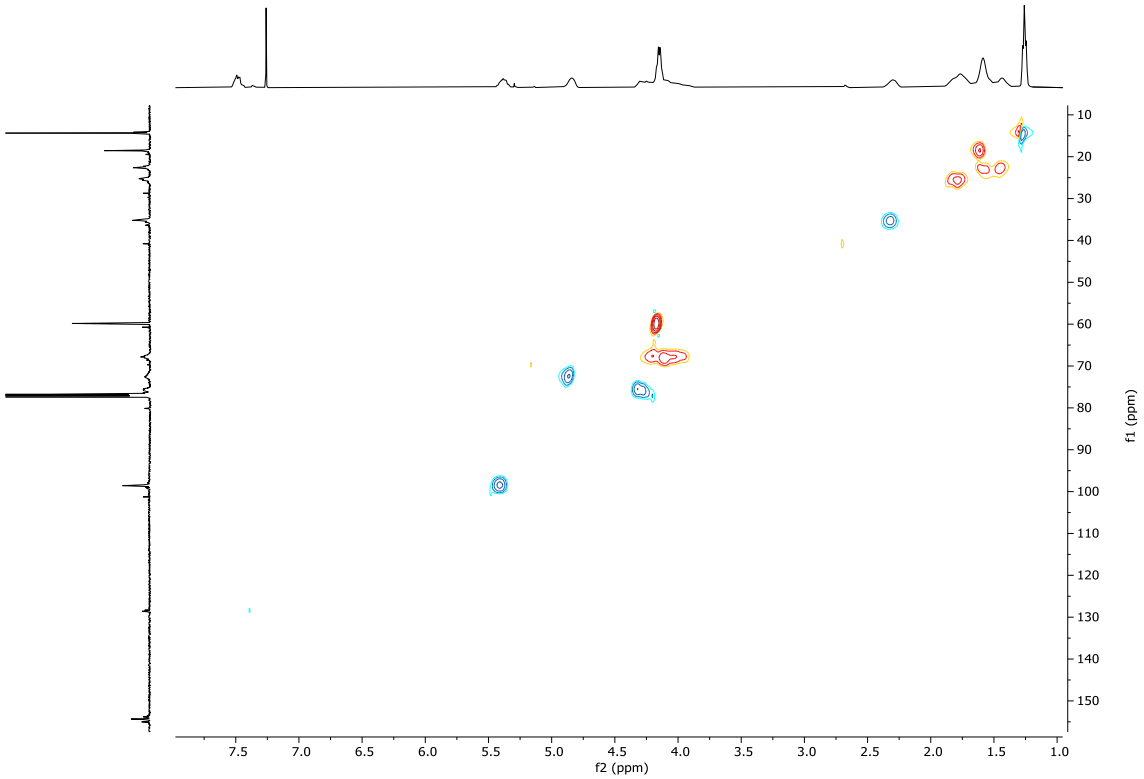


Figure S66*:* **^{1}H - ^{13}C HSQC** (500 MHz, $CDCl_3$) of **P6**

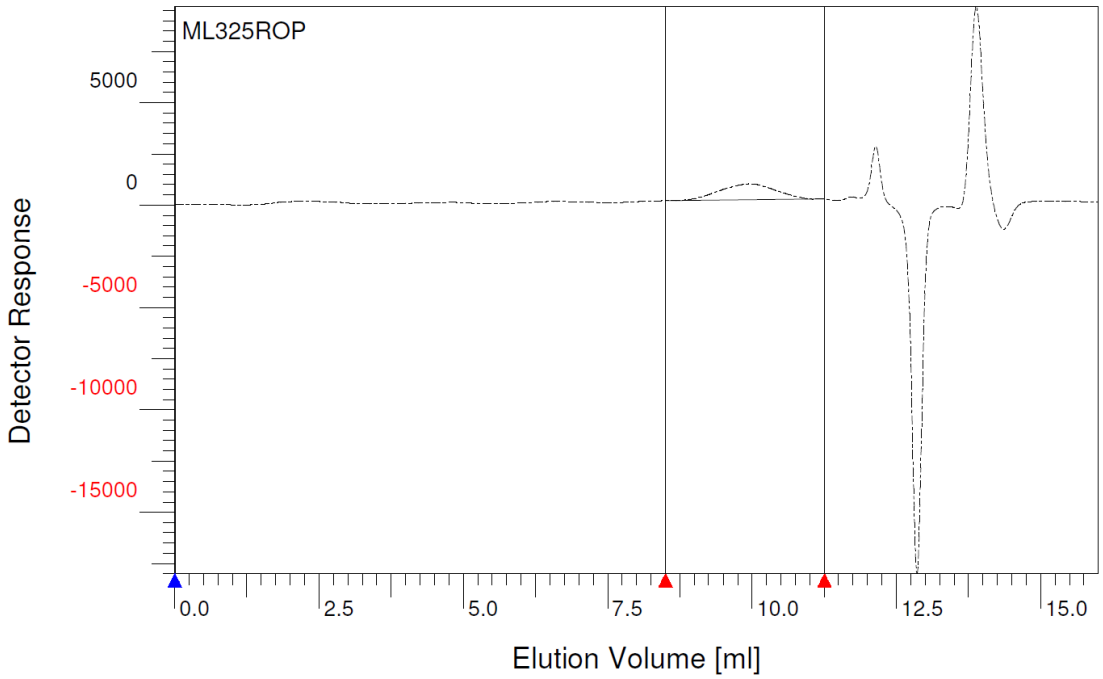


Figure S67: GPC analysis of **P6**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
5.0046e3	6.8430e3	9.3074e3	5.5097e3	1.3674

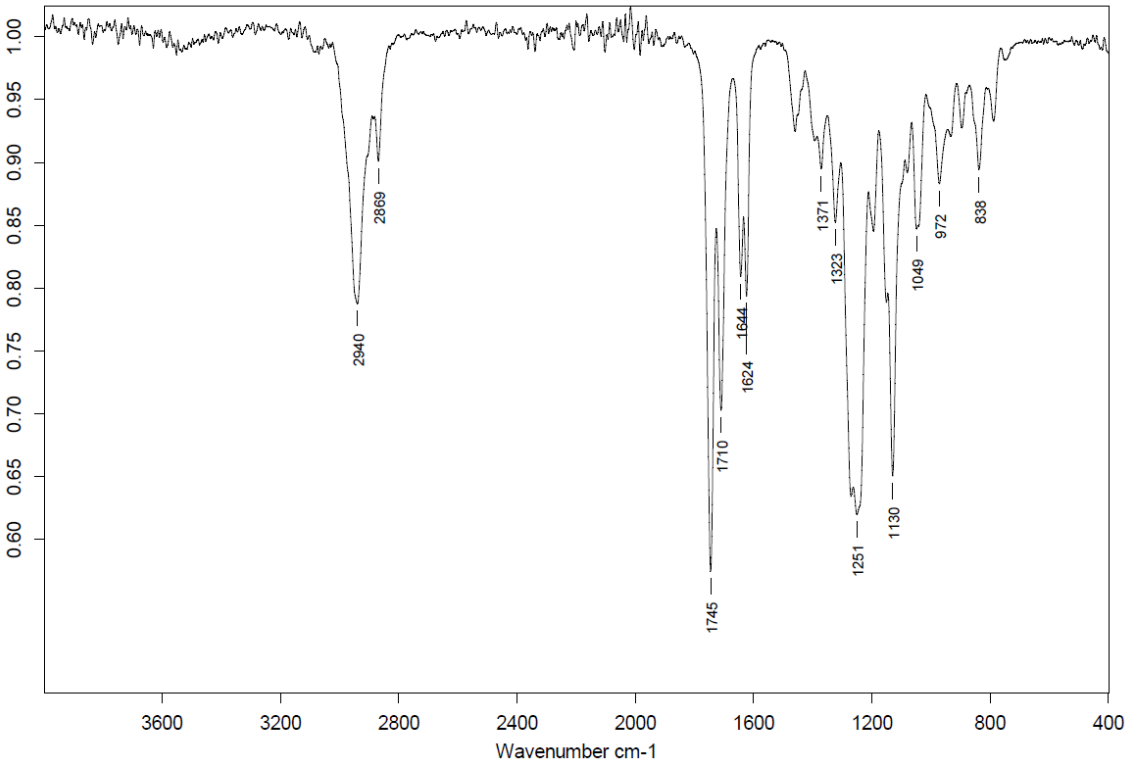


Figure S68: IR spectrum (neat) of **P6**

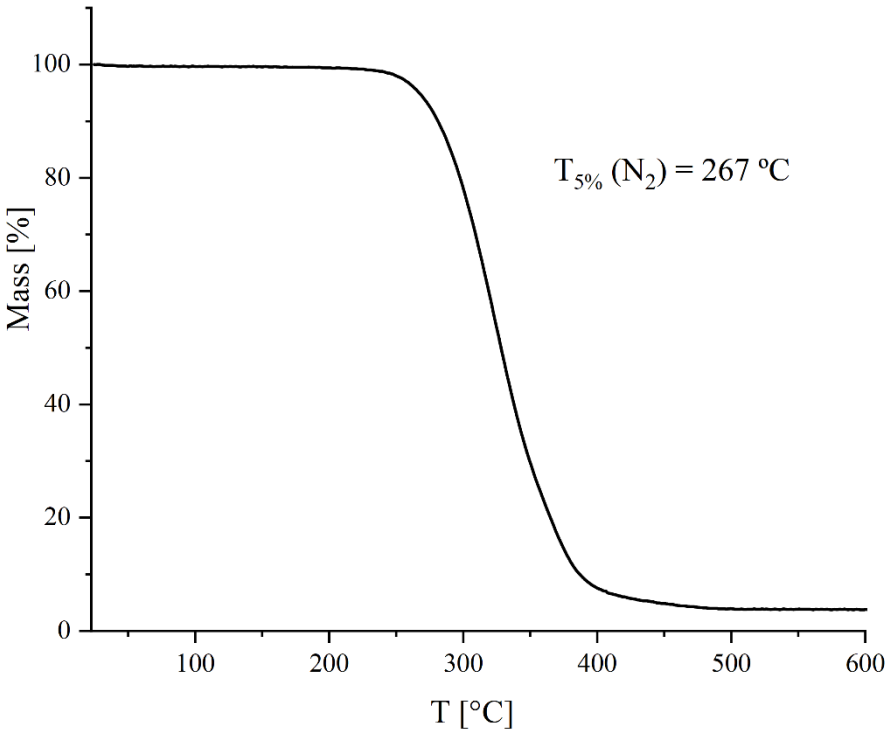


Figure S69: TGA thermogram of **P6**

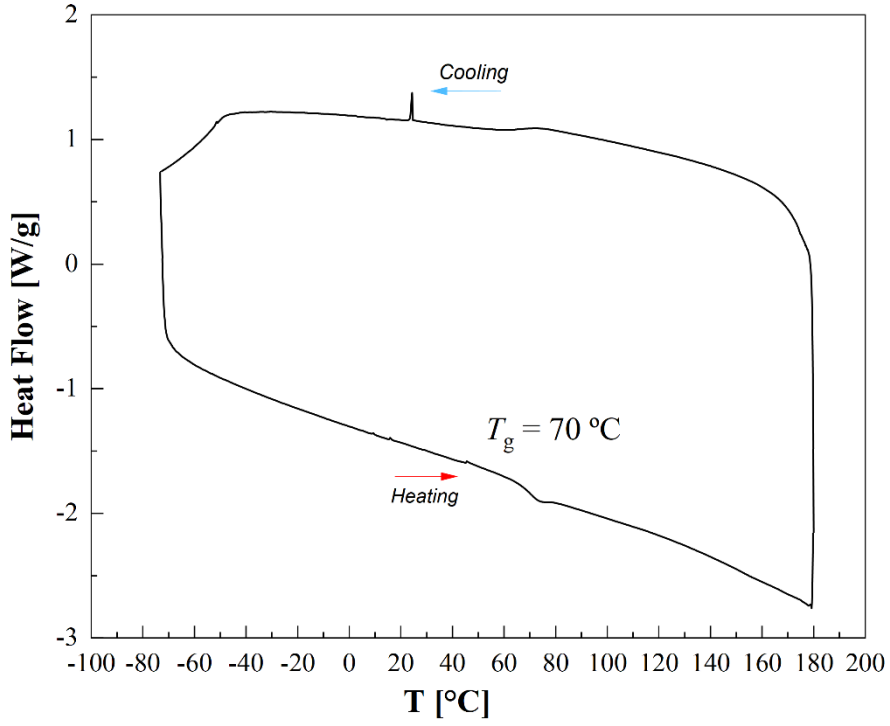


Figure S70: DSC thermogram of **P6**

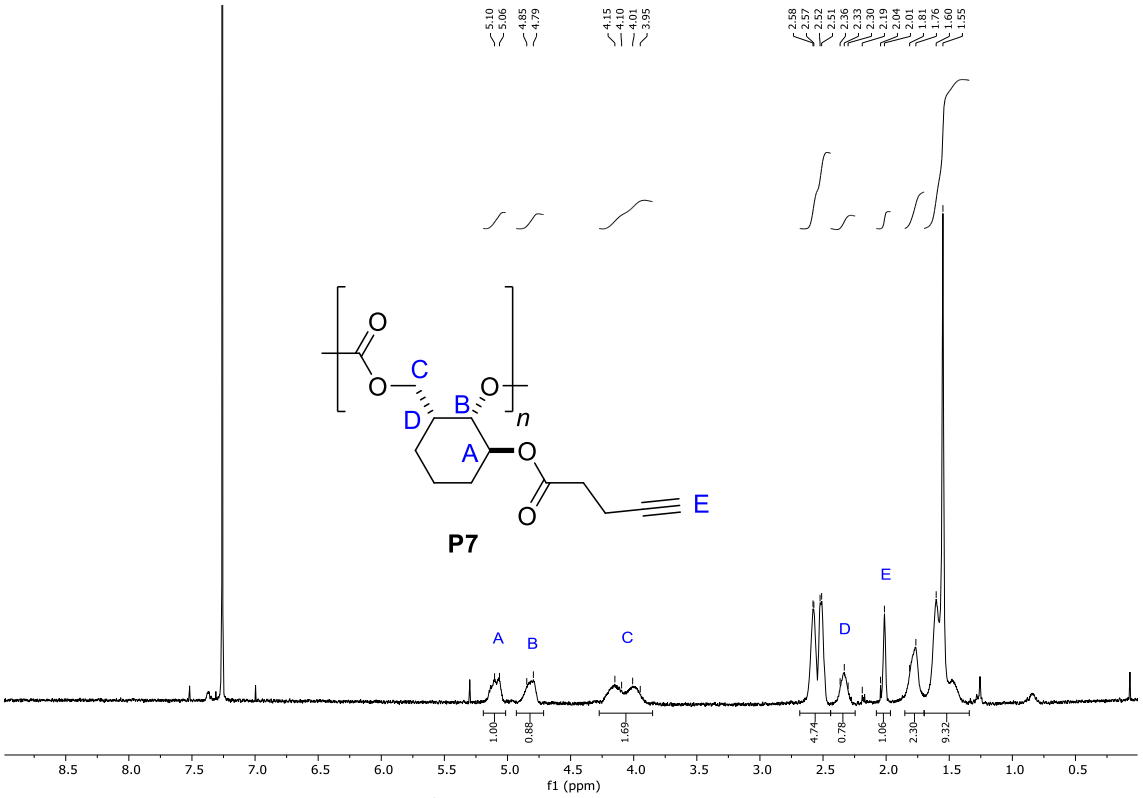


Figure S71: **^{1}H NMR** ($CDCl_3$, 400 MHz) of **P7**

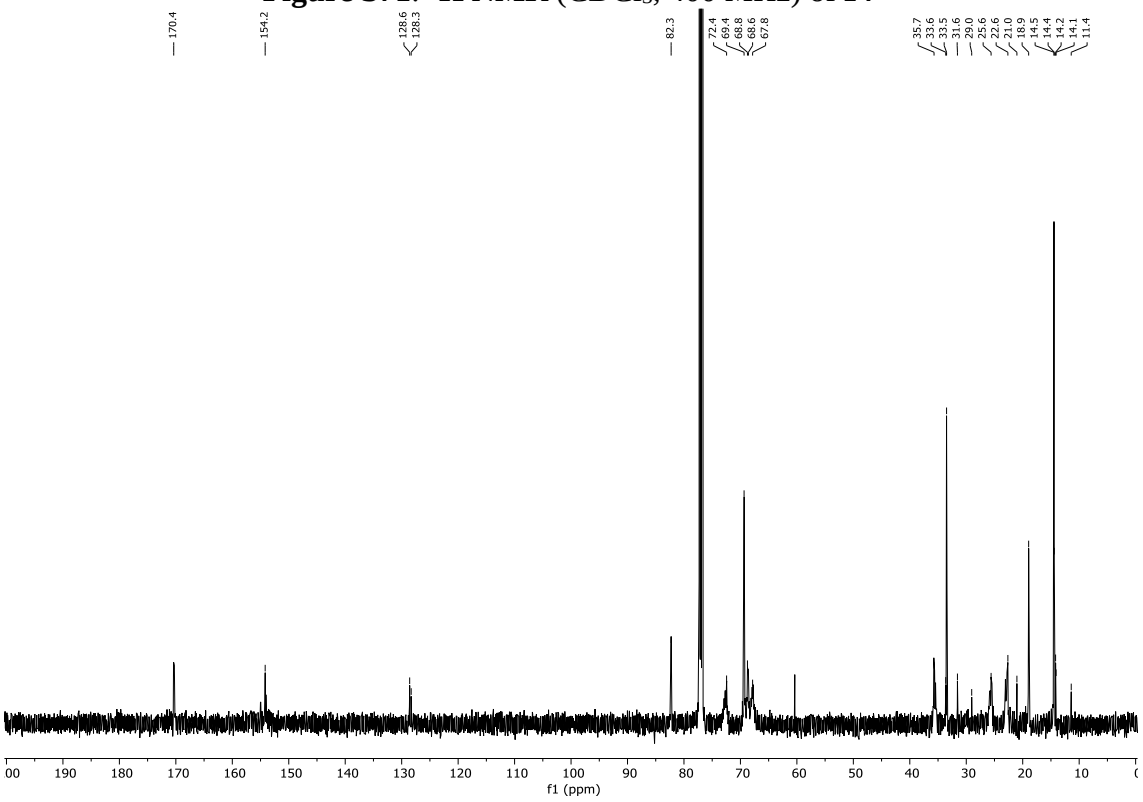


Figure S72: **^{13}C NMR** ($CDCl_3$, 101 MHz) of **P7**

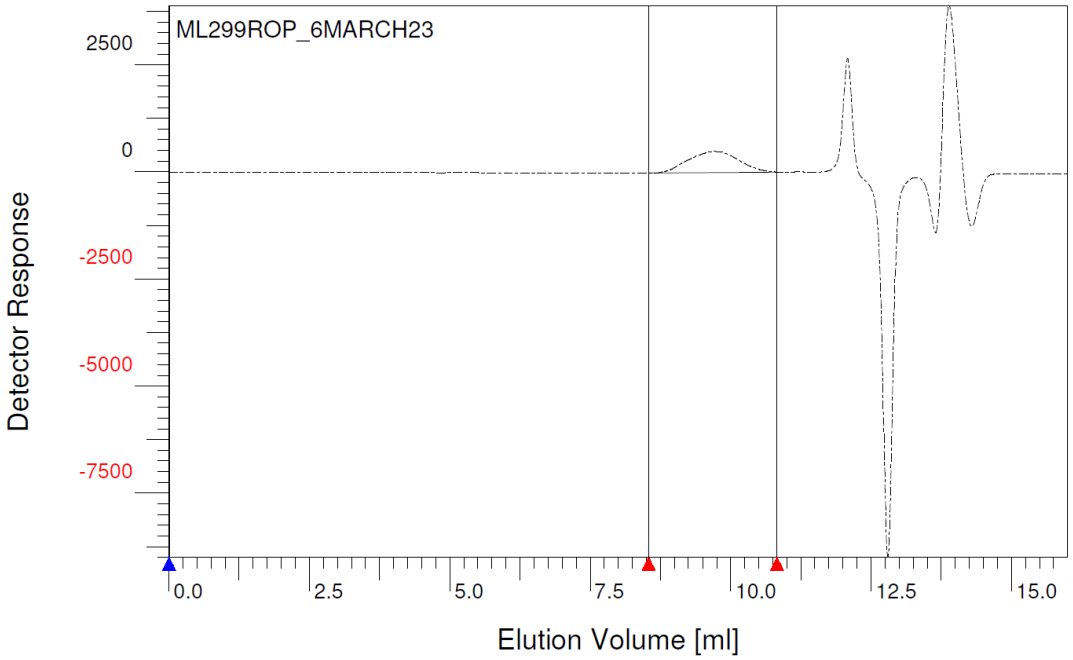


Figure S73: GPC analysis of **P7**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
6.8614e3	8.8848e3	1.1355e4	7.5927e3	1.2949

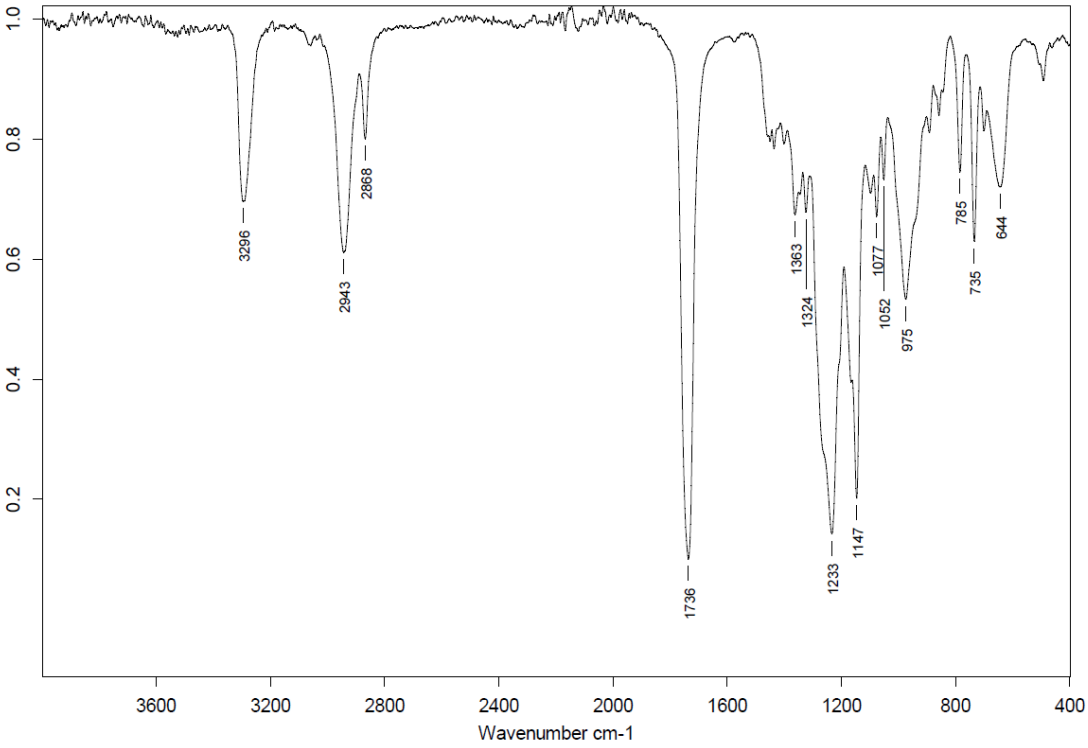


Figure S74: IR spectrum (neat) of **P7**

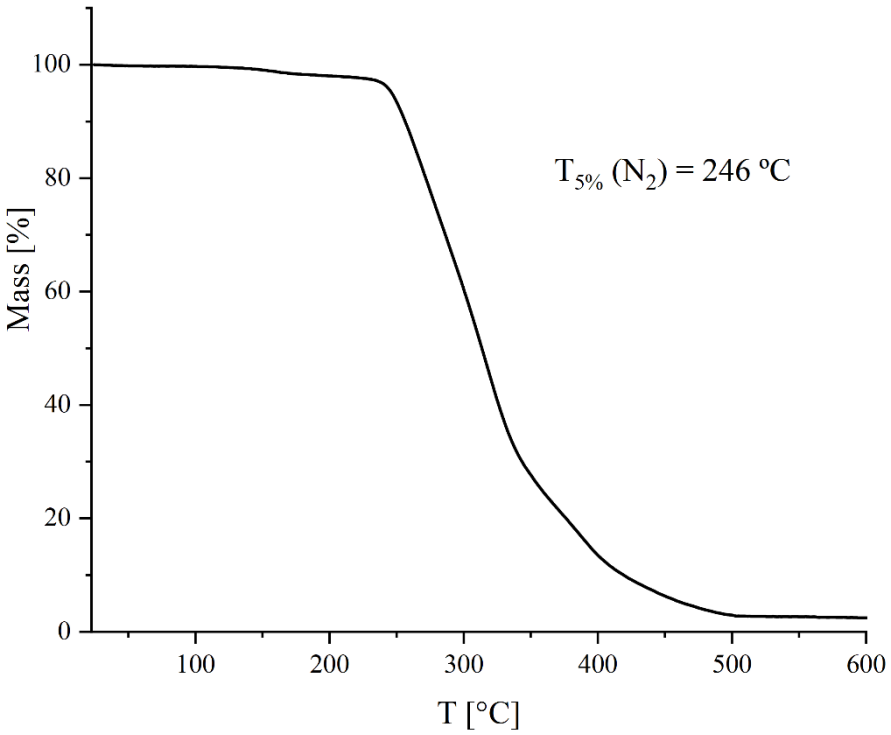


Figure S75: TGA thermogram of **P7**

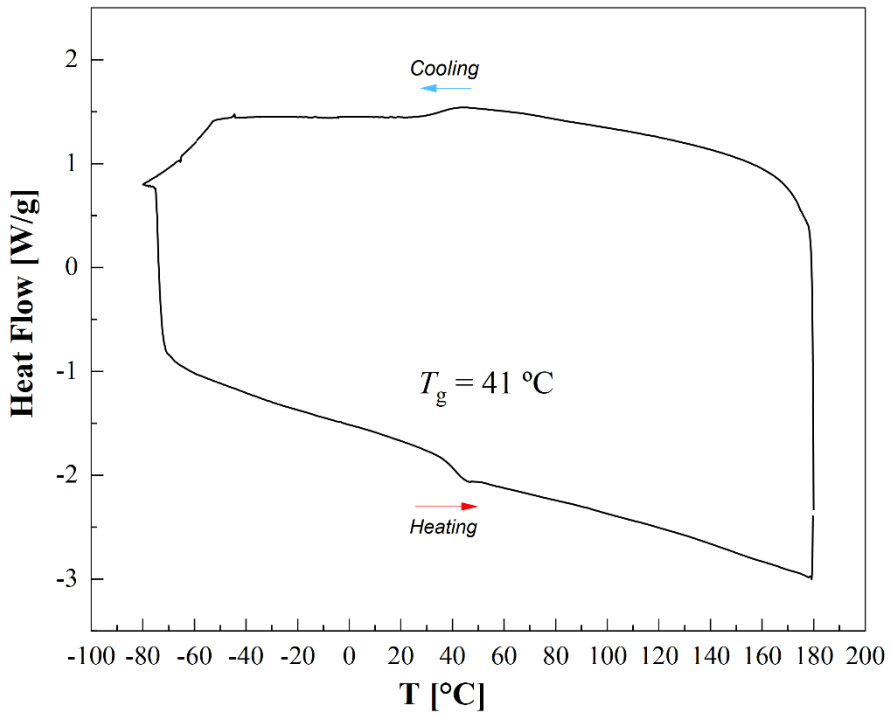


Figure S76: DSC thermogram of **P7**

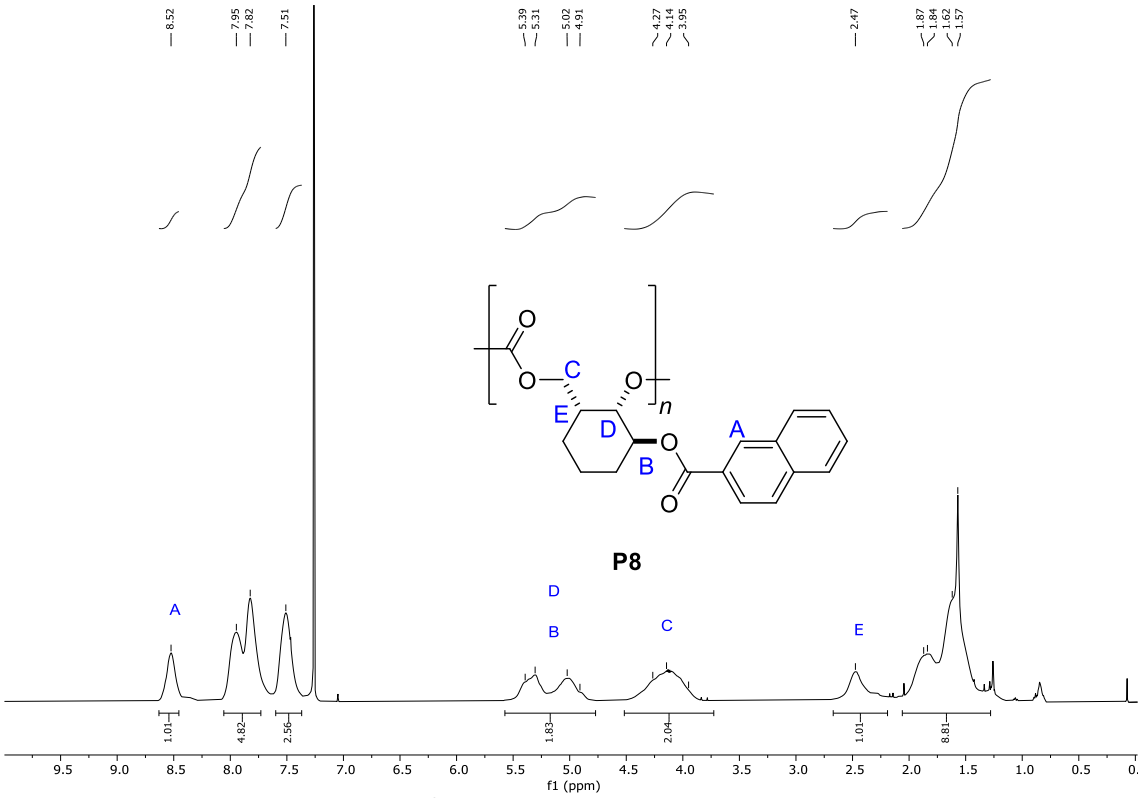


Figure S77: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P8**

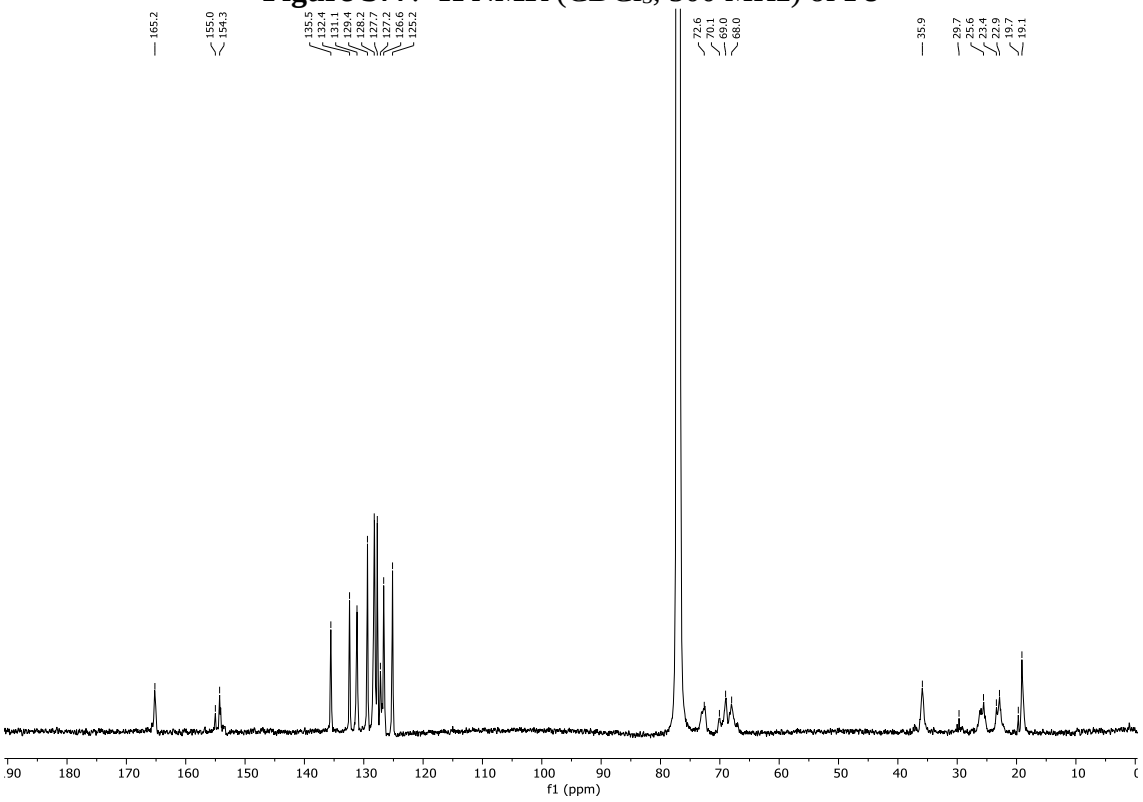


Figure S78: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P8**

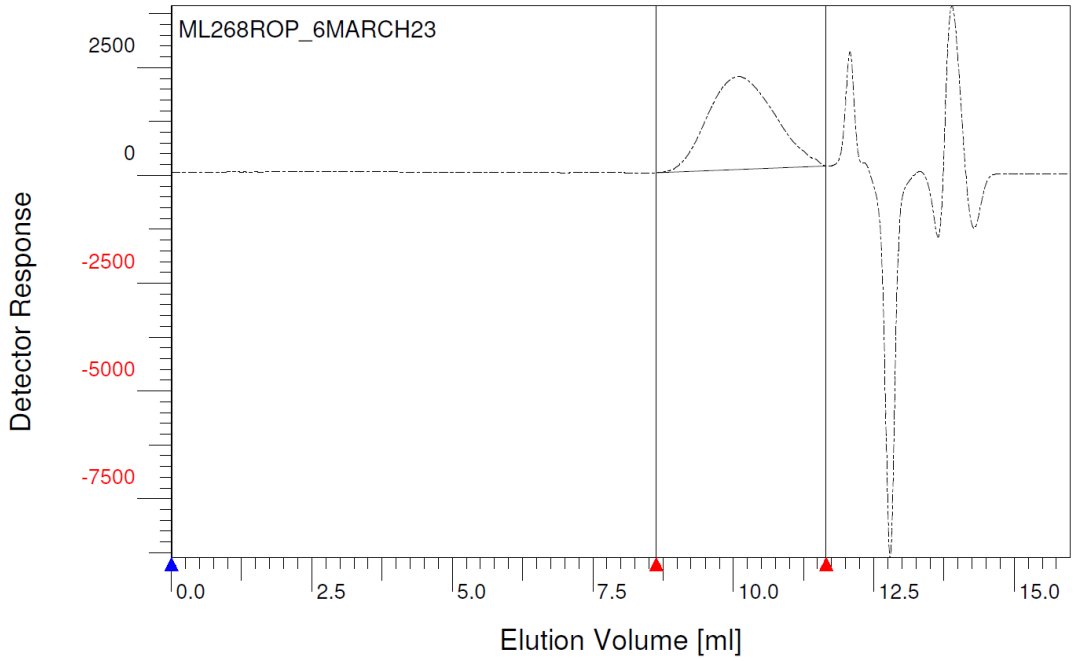


Figure S79: GPC analysis of **P8**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
3.2448e3	5.2217e3	7.7096e4	4.6660e3	1.6093

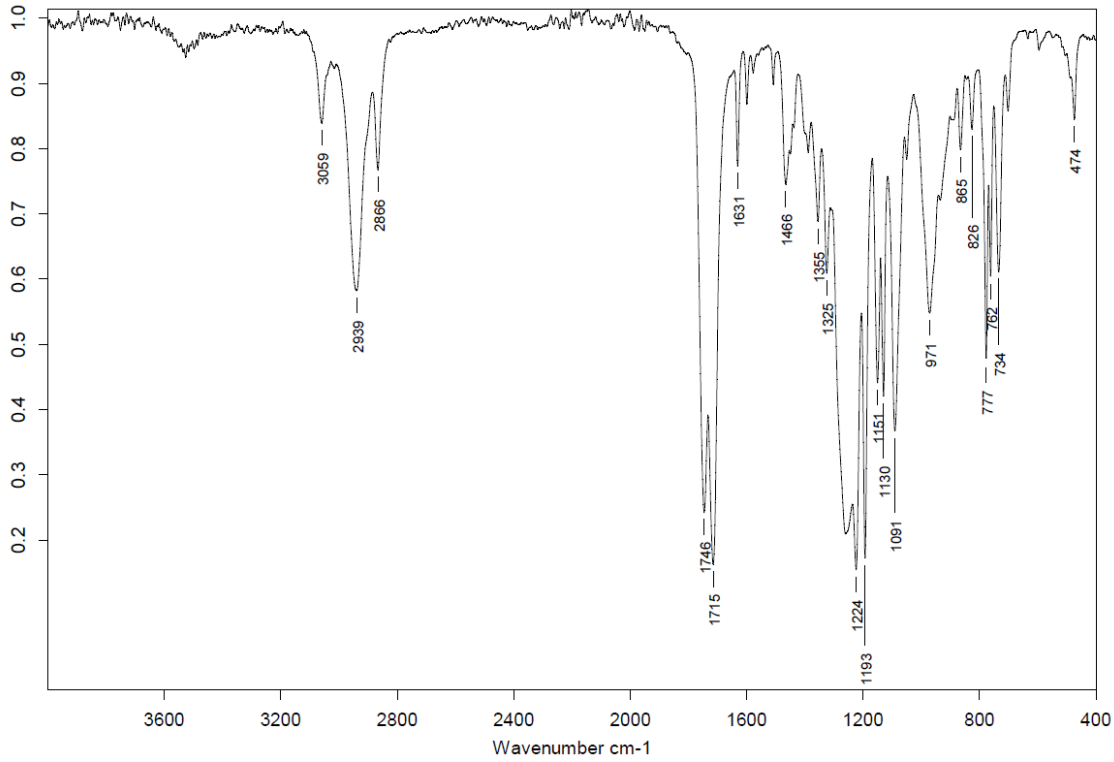


Figure S80: IR spectrum (neat) **P8**

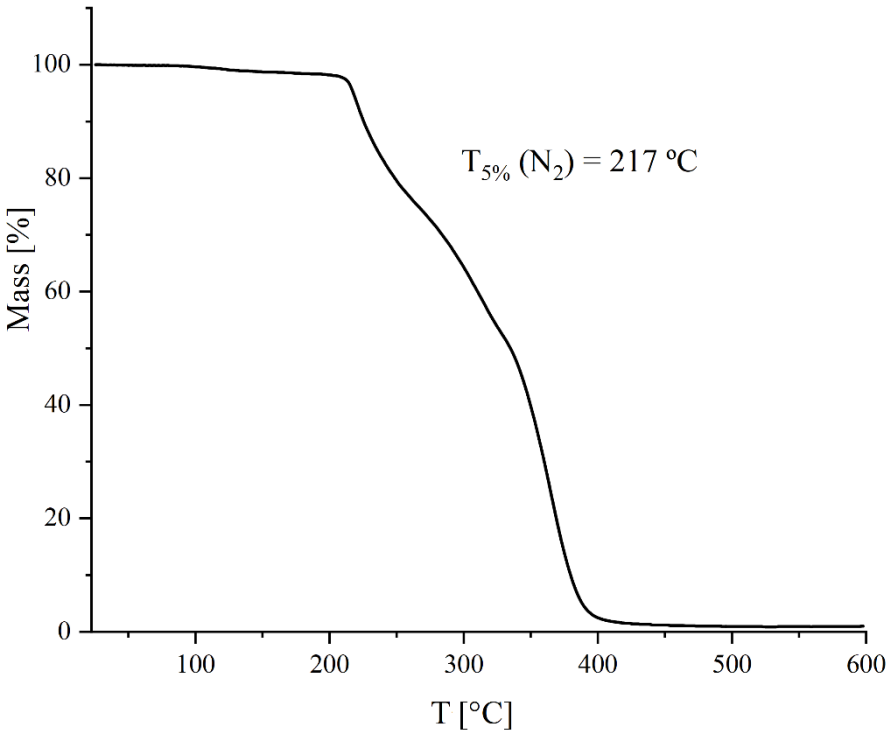


Figure S81: TGA thermogram of **P8**

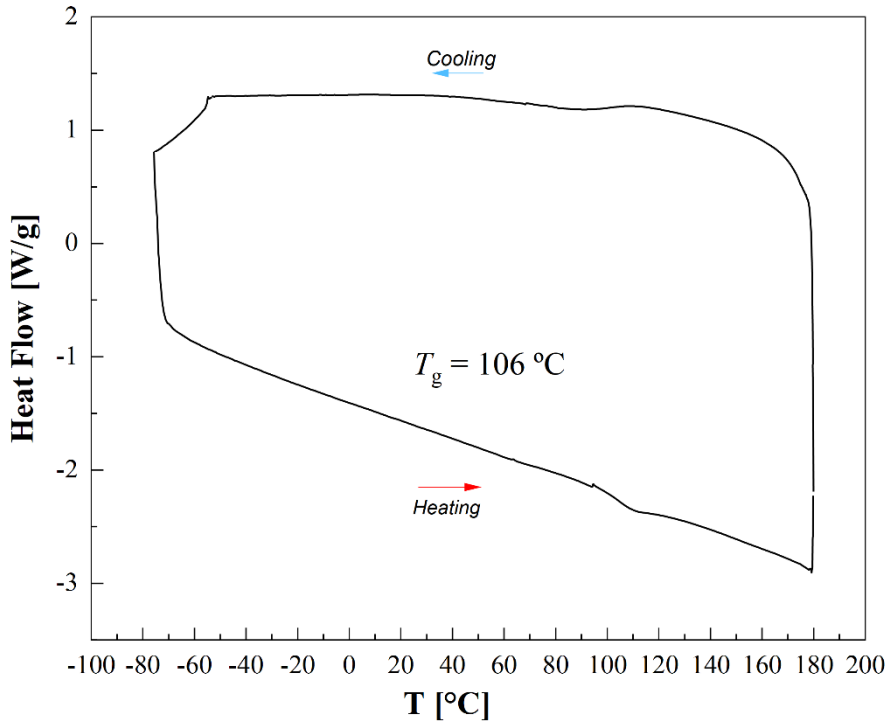


Figure S82: DSC thermogram of **P8**

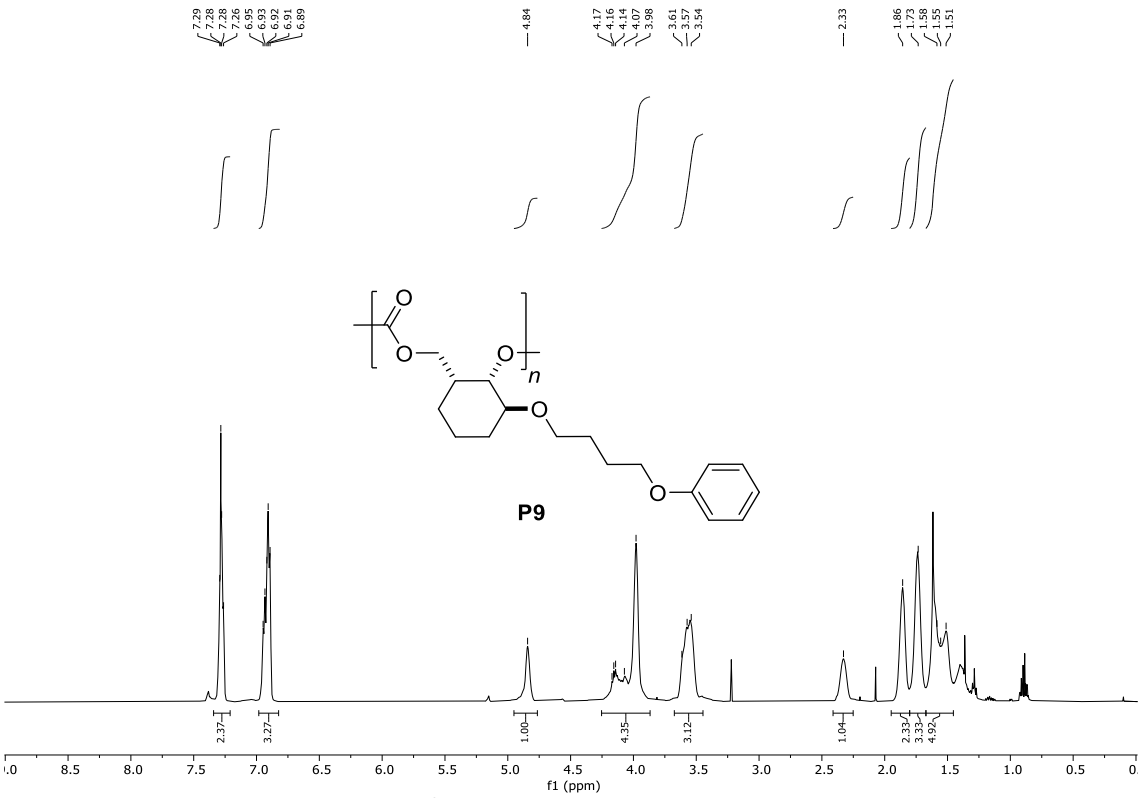


Figure S83: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P9**

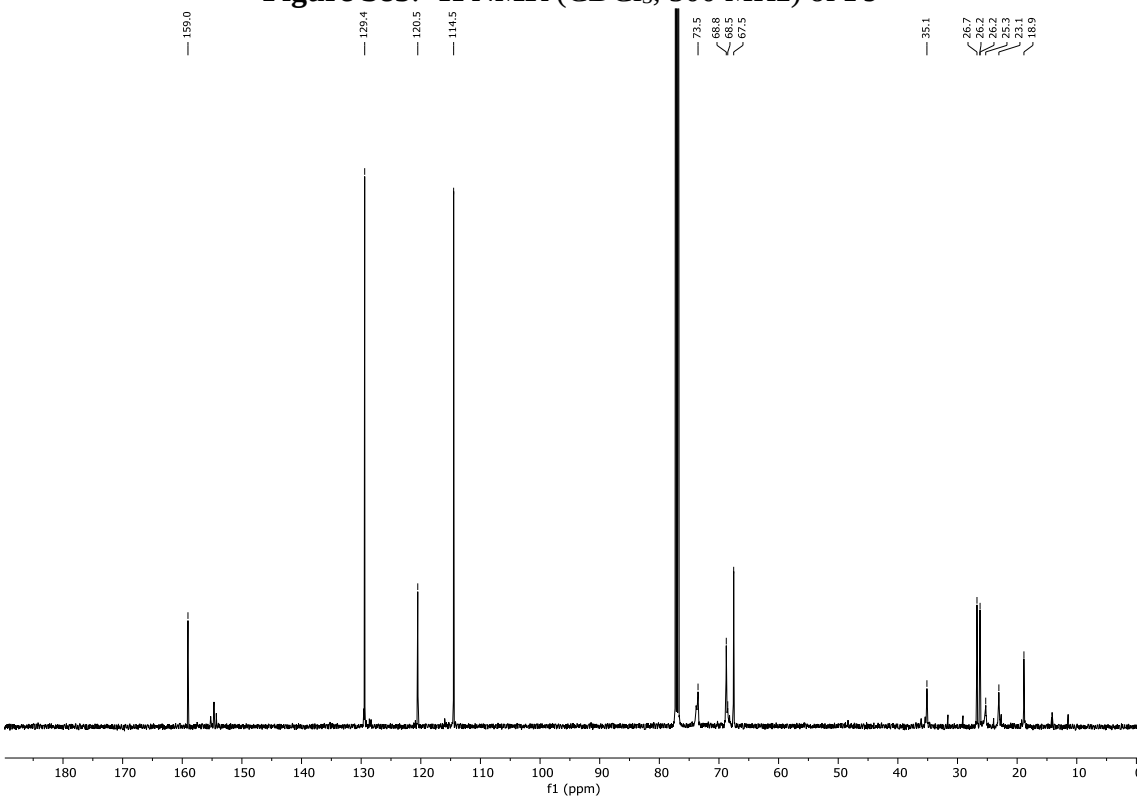


Figure S84: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P9**

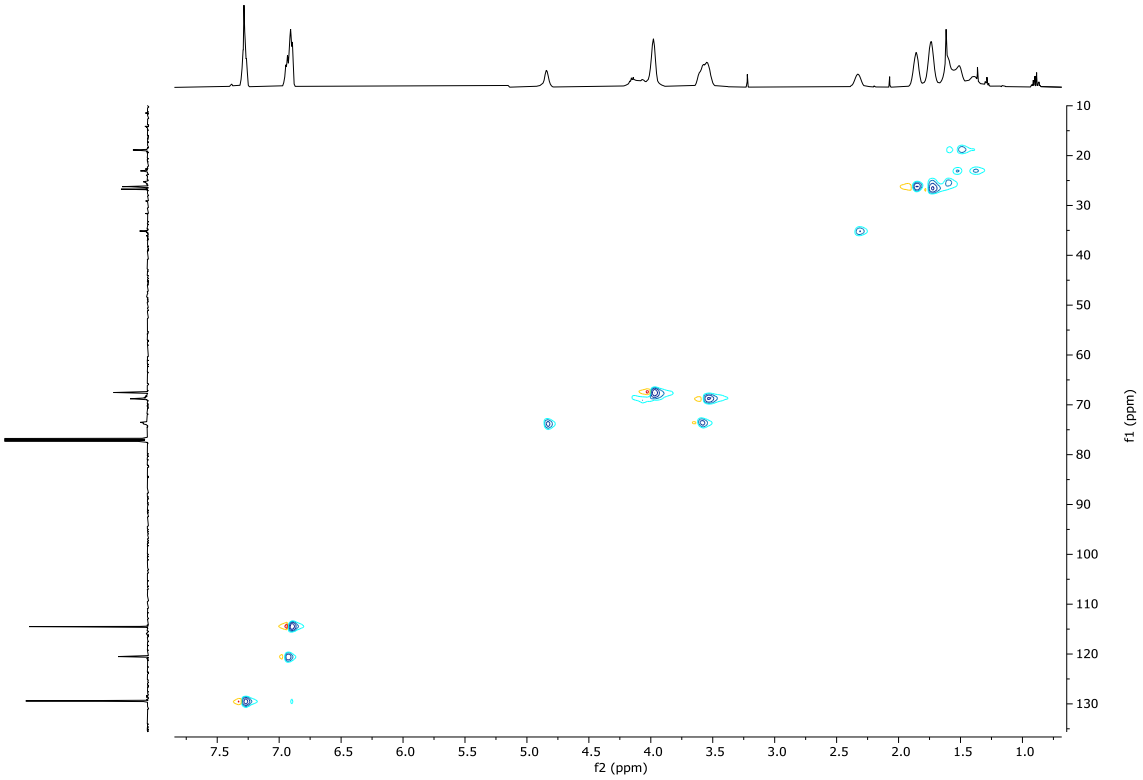


Figure S85: **^{1}H-^{13}C HSQC** ($CDCl_3$, 500 MHz) of **P9**

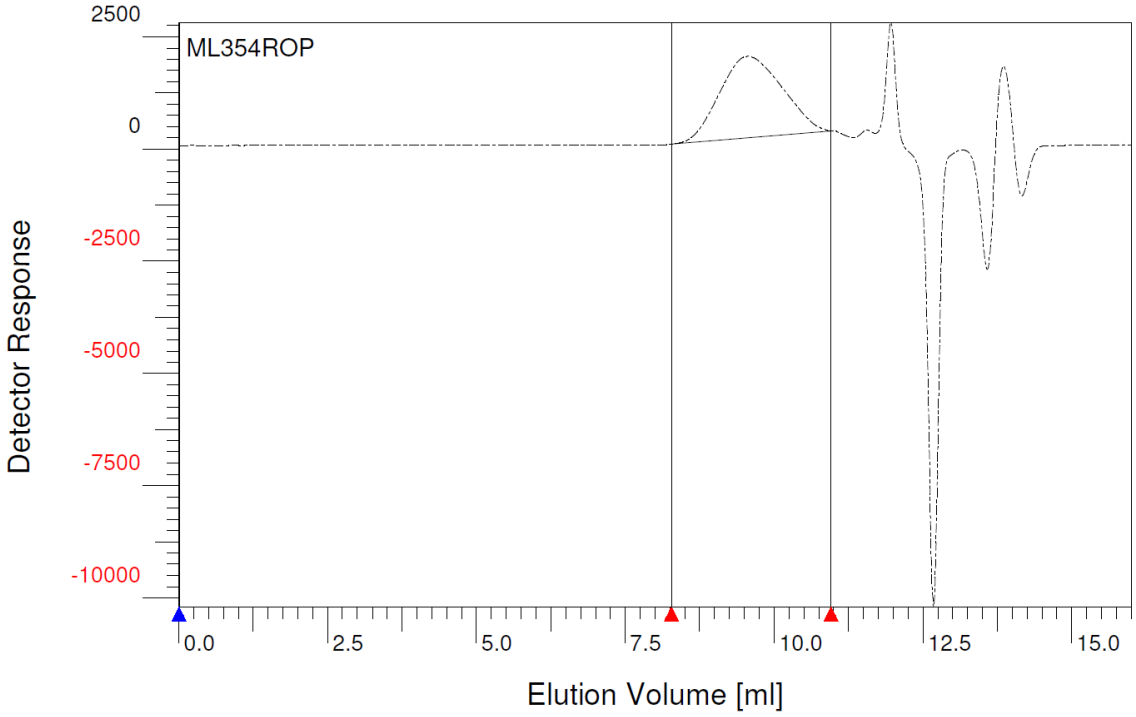


Figure S86: GPC analysis of **P9**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
7.0639e3	1.0201e4	1.4229e4	9.4835e3	1.4441

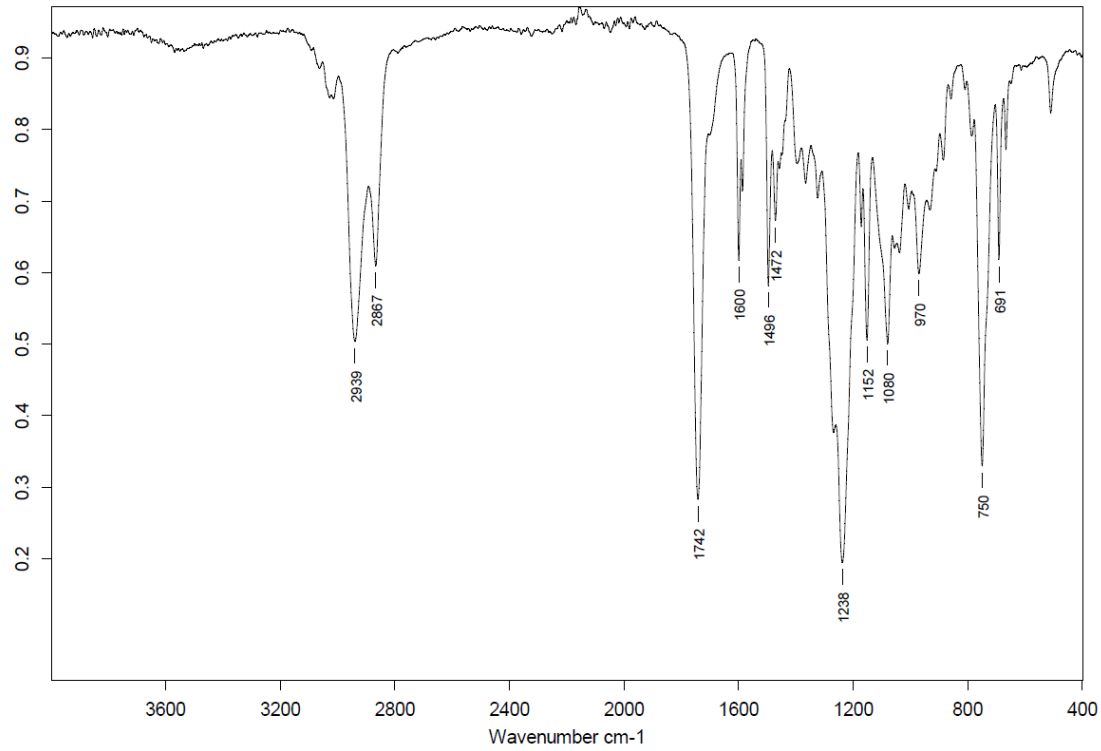


Figure S87: IR spectrum (neat) of **P9**

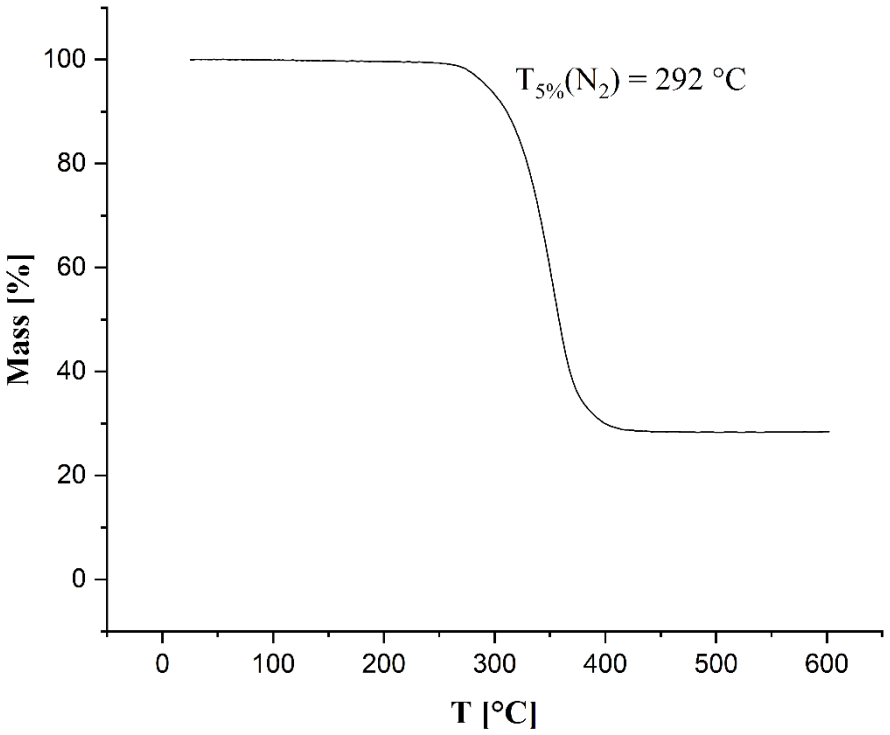


Figure S88: TGA thermogram of **P9**

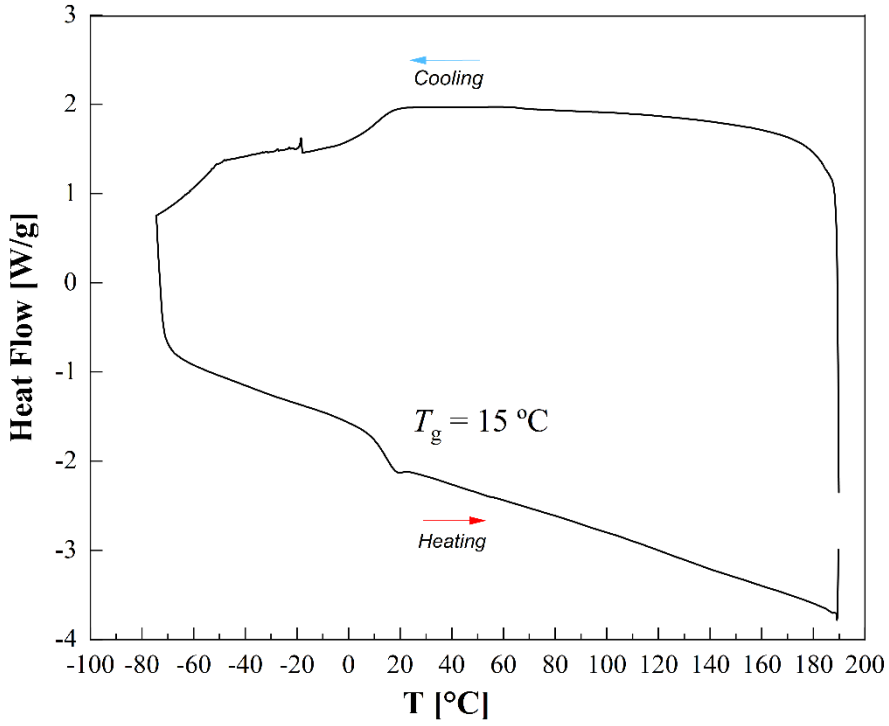


Figure S89: DSC thermogram of **P9**

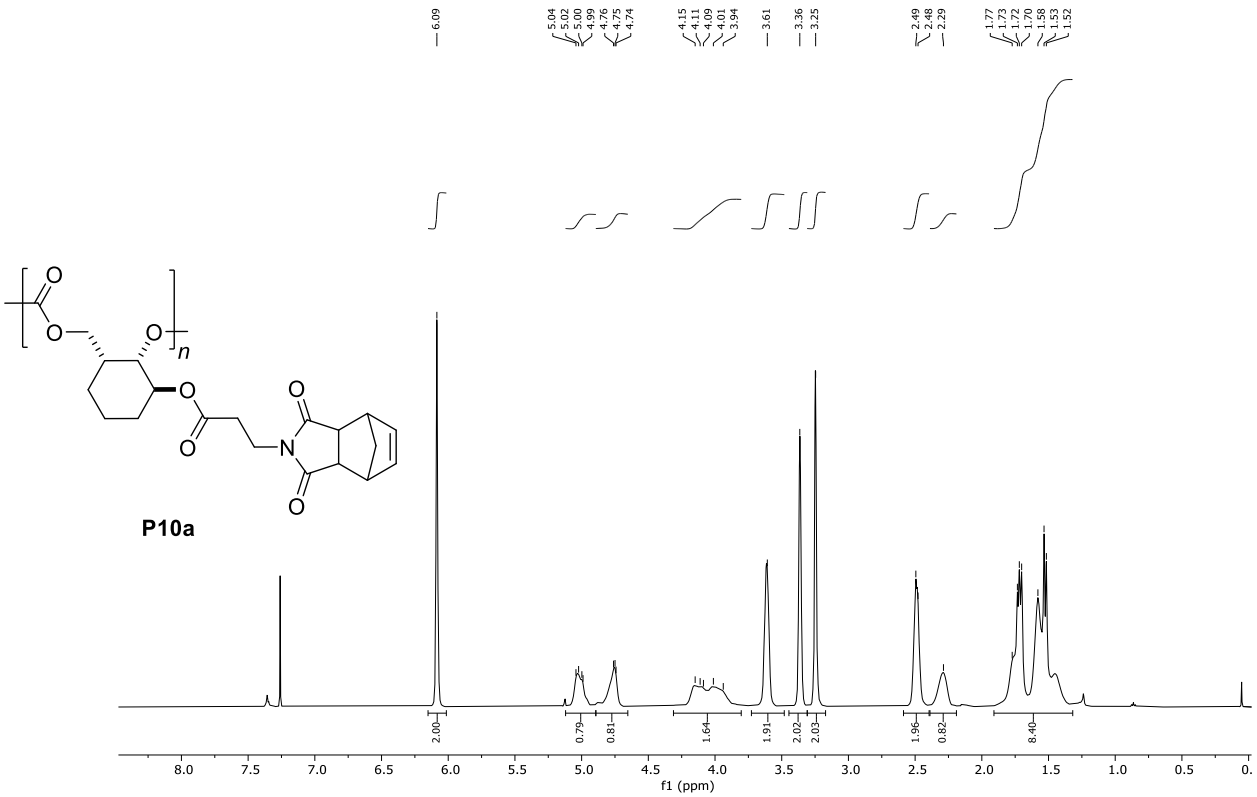


Figure S90: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P10a**

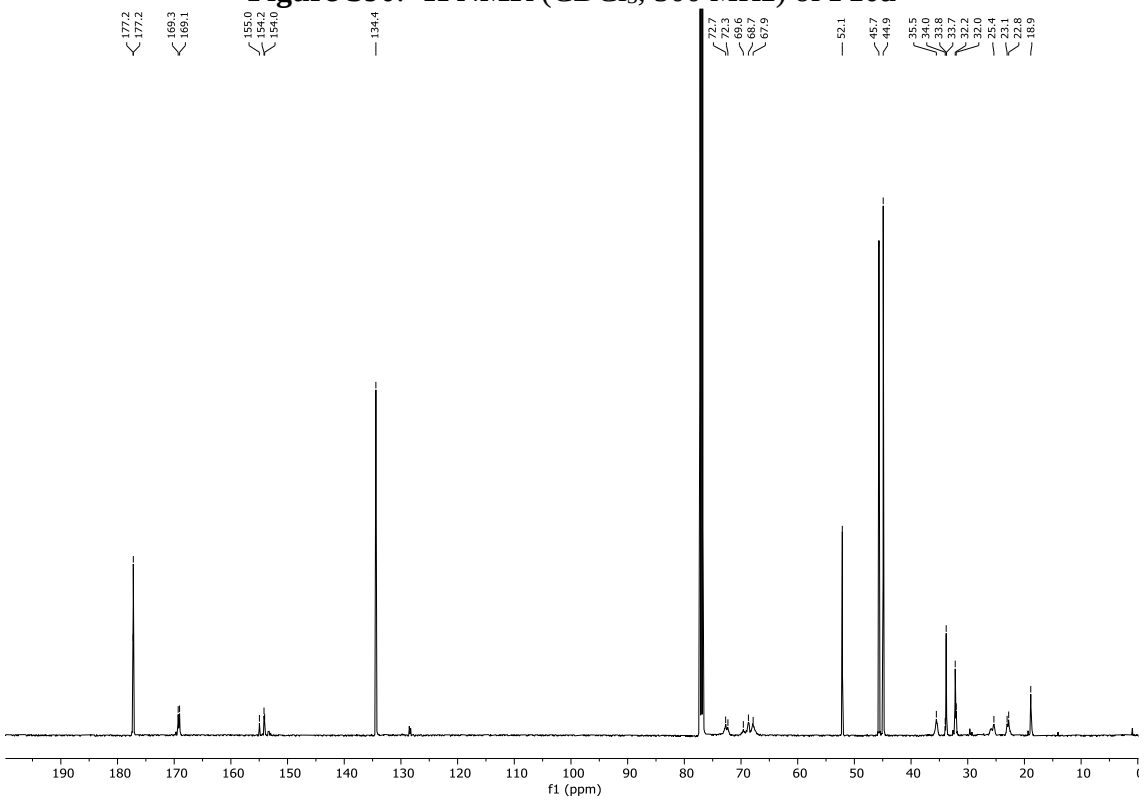


Figure S91: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P10a**

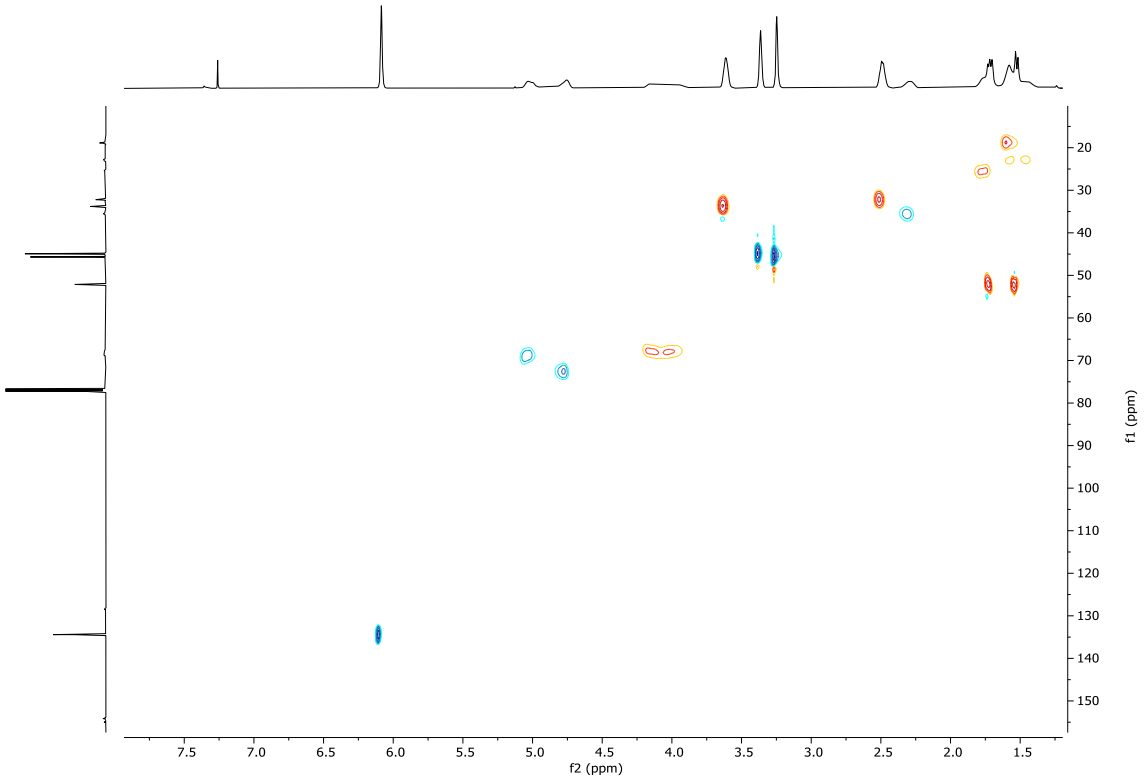


Figure S92: **^{1}H-^{13}C HSQC** ($CDCl_3$, 500HMz) of **P10a**

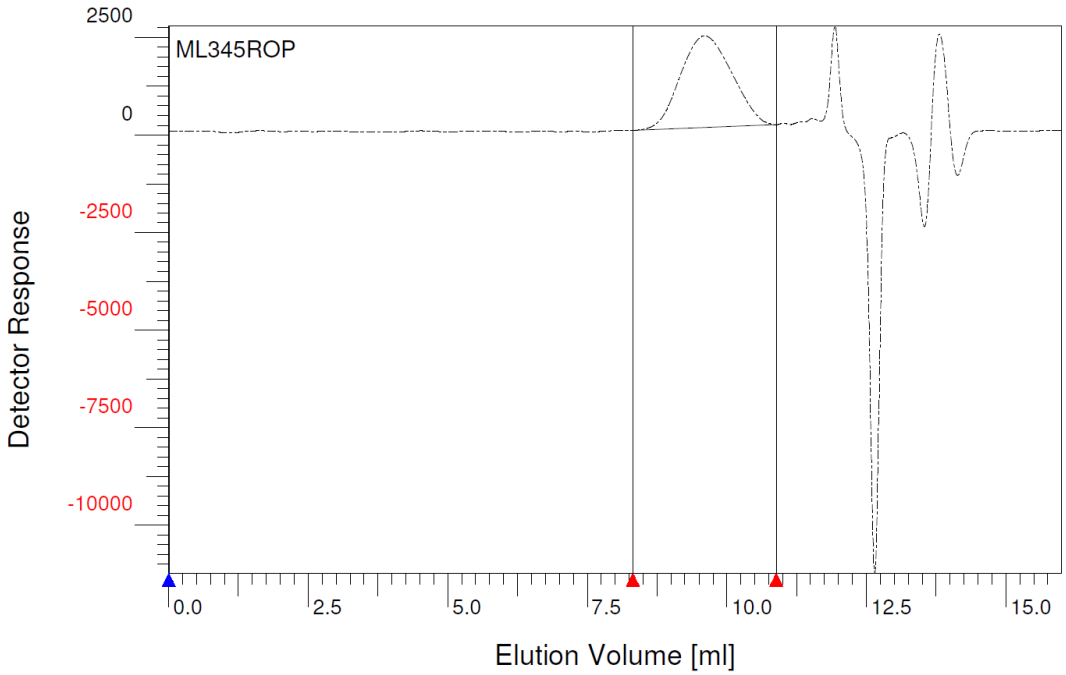


Figure S93: GPC analysis of **P10a**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
7.2324e3	9.6396e3	1.2686e4	8.8592e3	1.3328

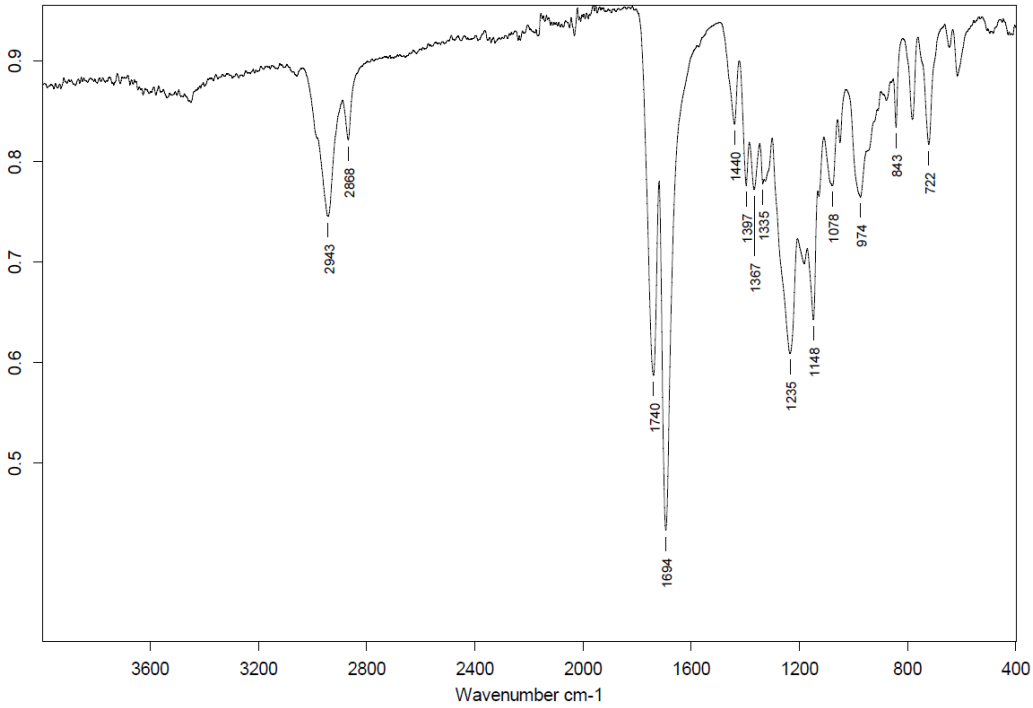


Figure S94: IR spectrum (neat) of **P10a**

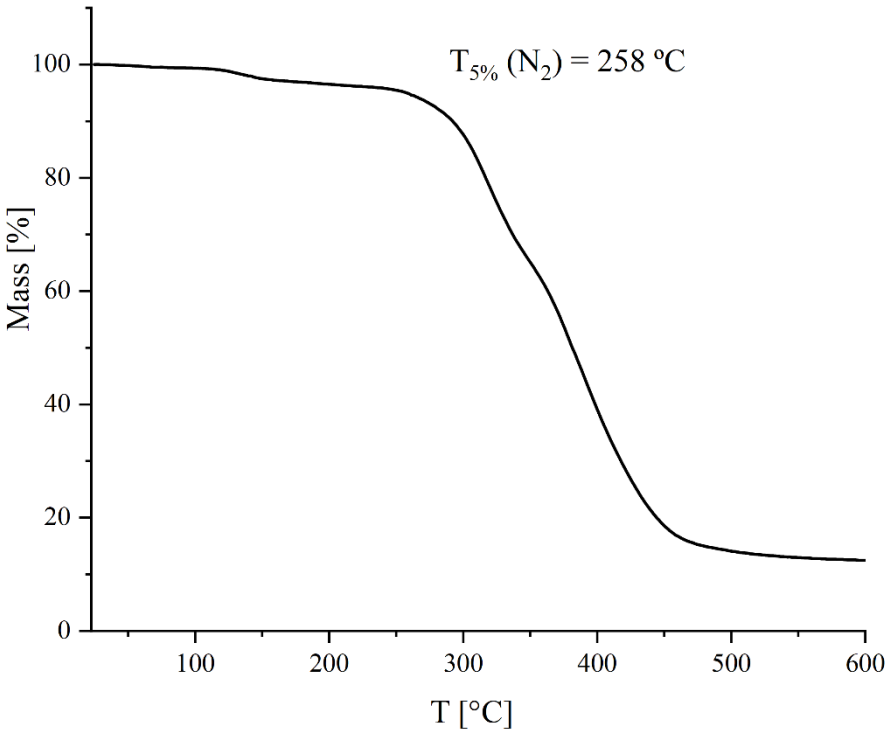


Figure S95: TGA thermogram of **P10a**

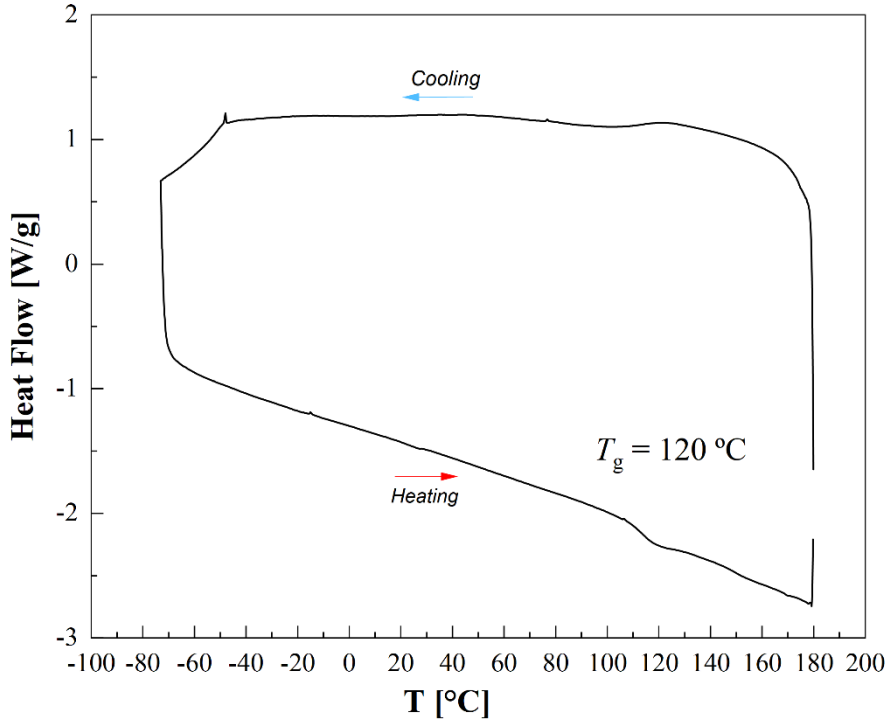


Figure S96: DSC thermogram of **P10a**

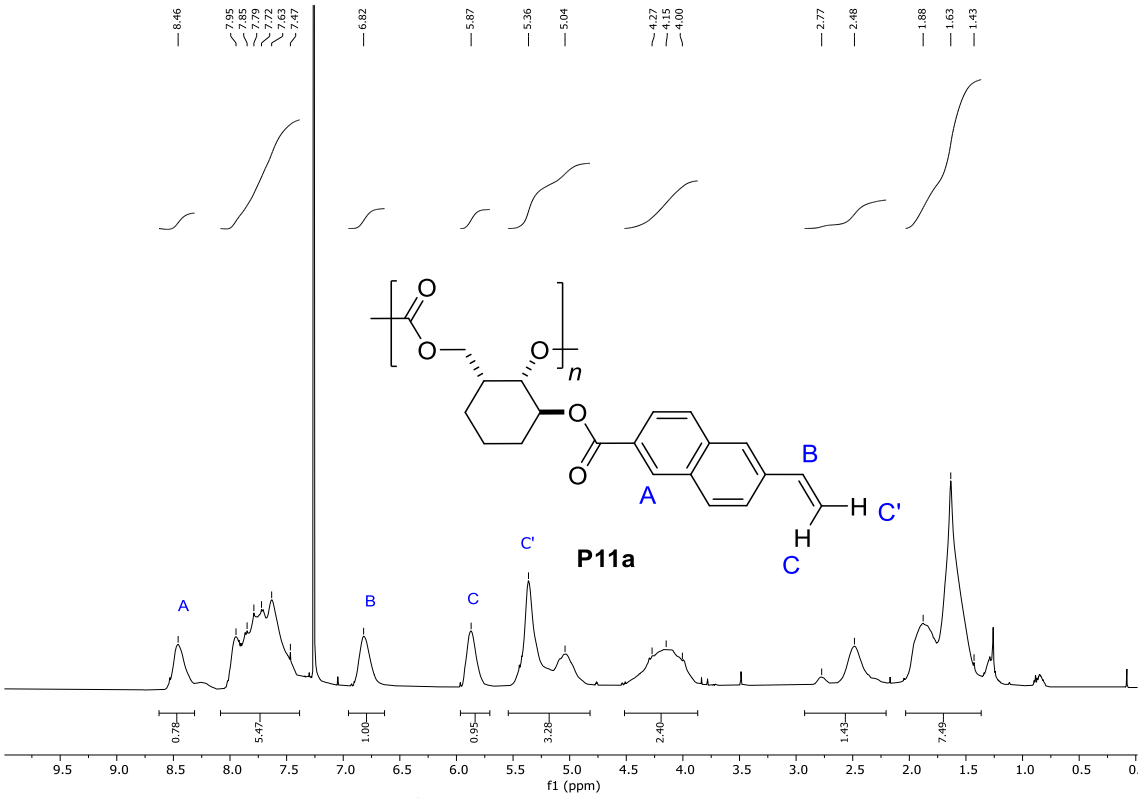


Figure S97: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **P11a**

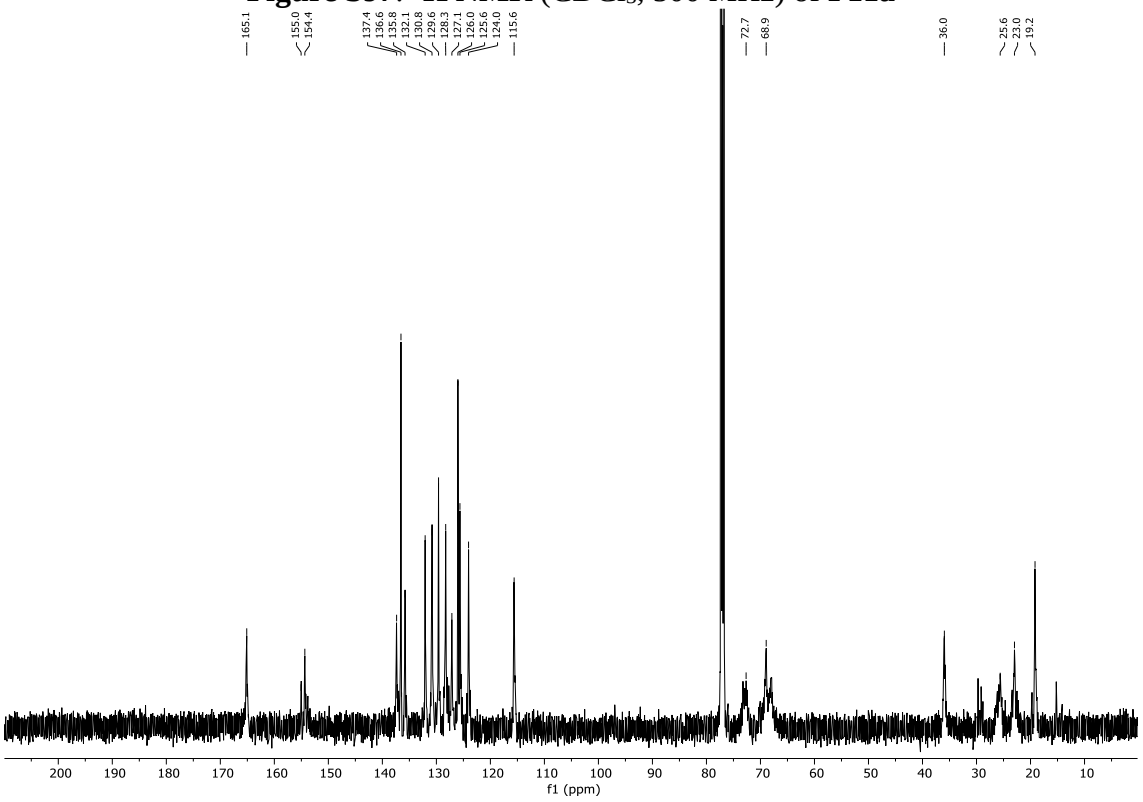


Figure S98: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P11a**

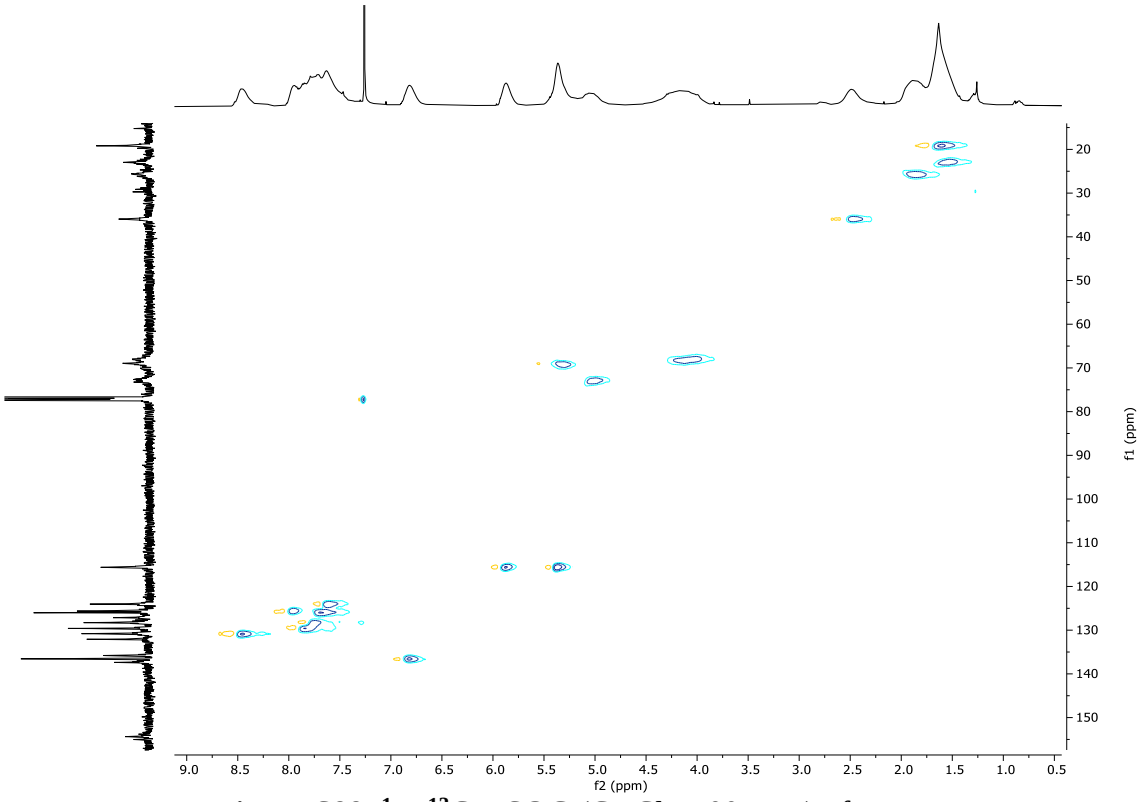


Figure S99: **^{1}H-^{13}C HSQC** ($CDCl_3$, 500MHz) of **P11a**

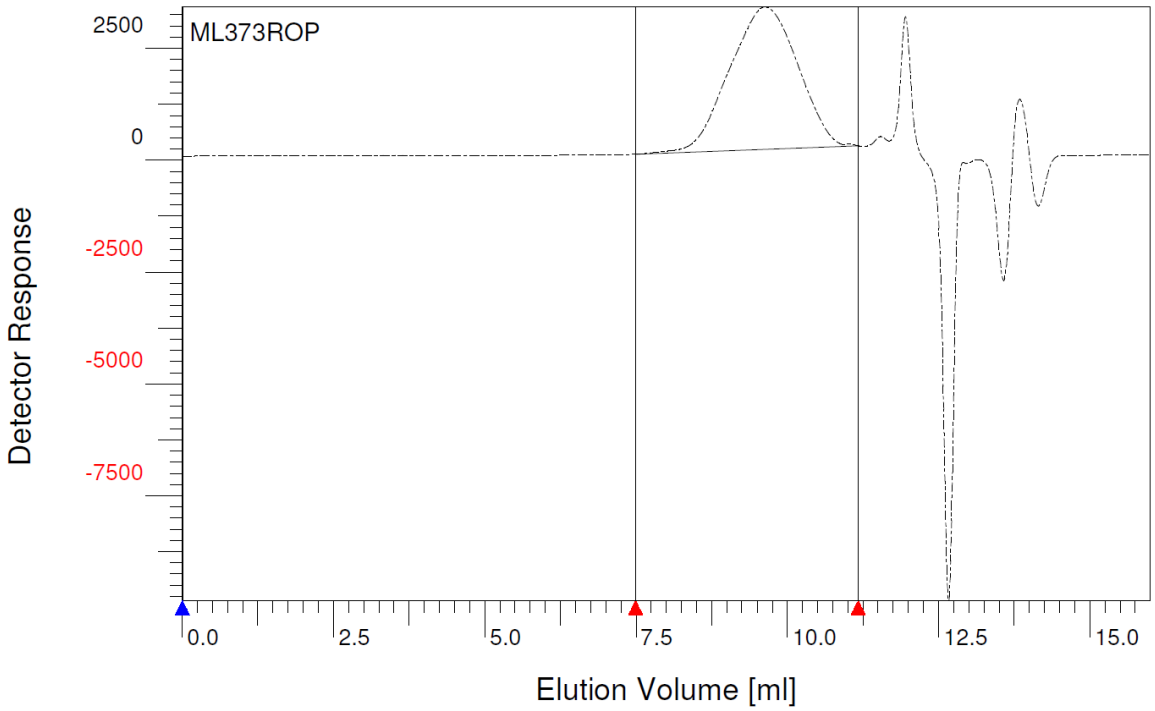


Figure S100: GPC analysis of **P11a**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
7.1865e3	1.1461e4	1.9662e4	8.4401e3	1.5947

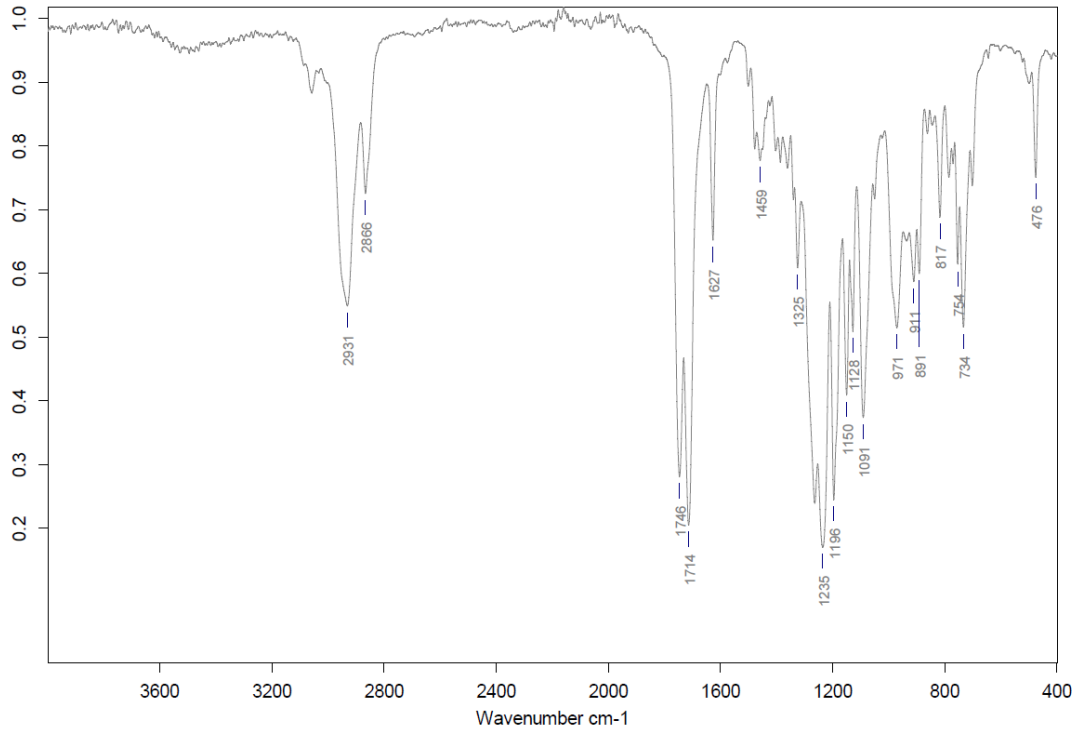


Figure S101: IR spectrum (neat) of **P11a**

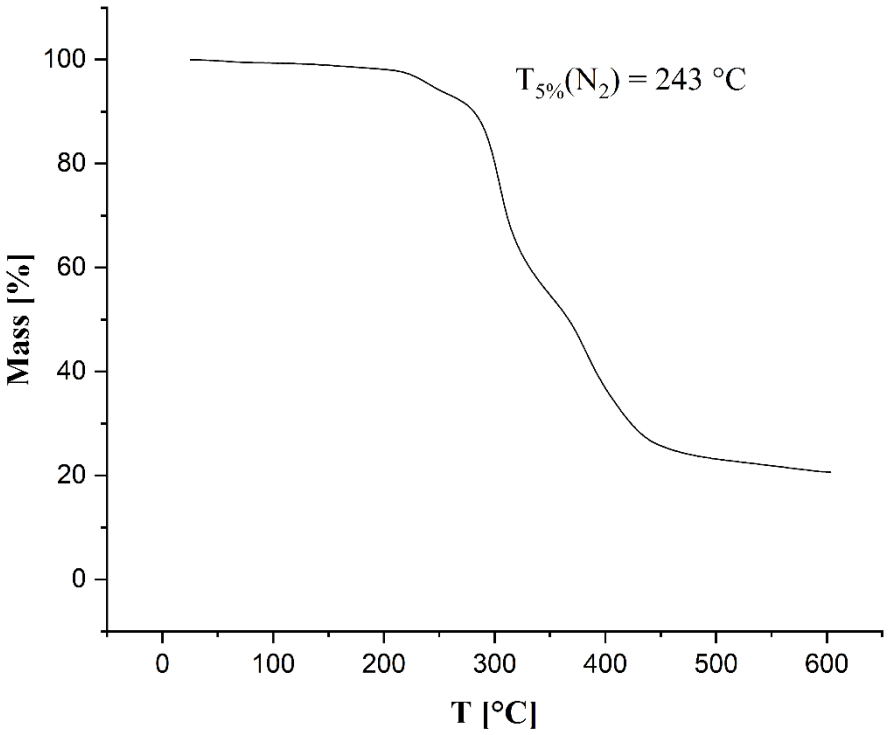


Figure S102: TGA thermogram of **P11a**

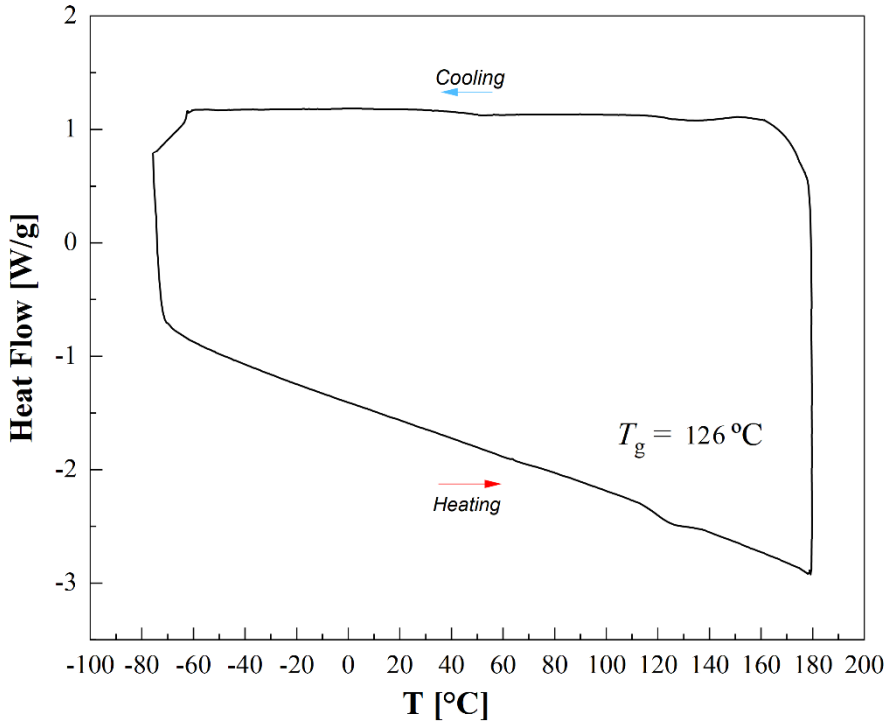


Figure S103: DSC thermogram of **P11a**

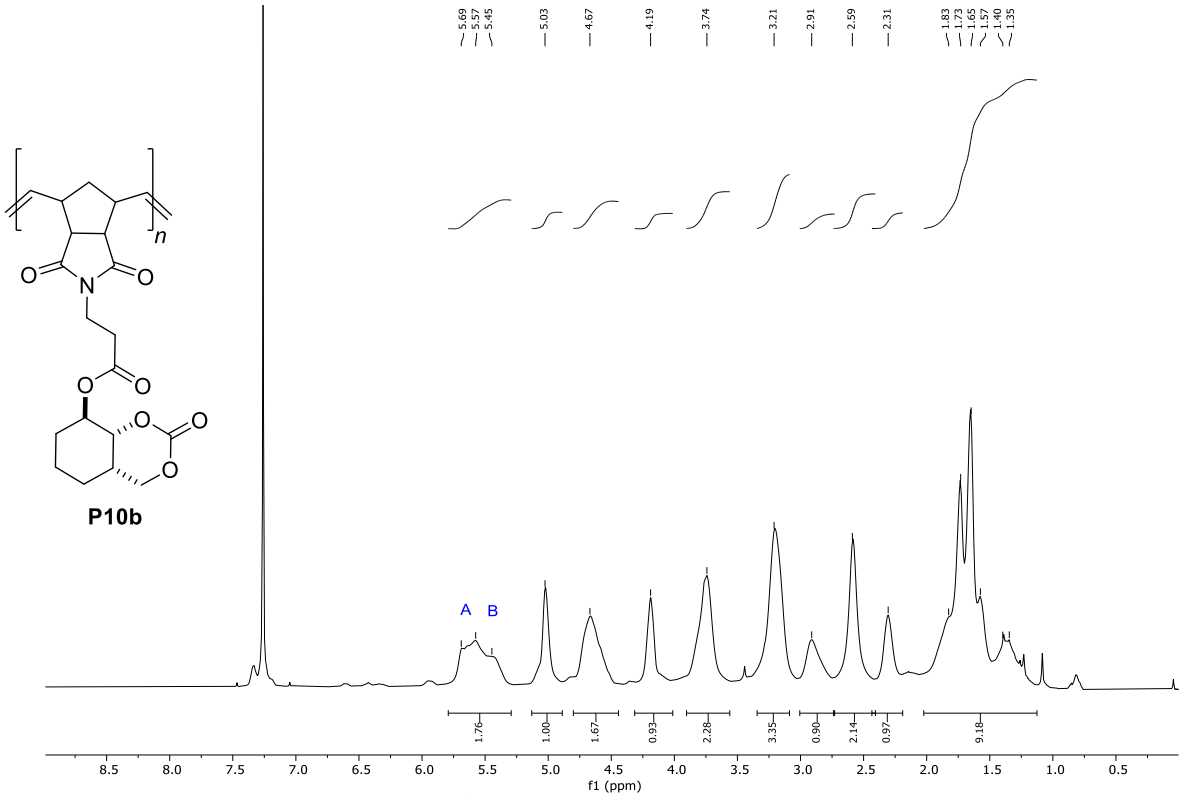


Figure S104: **^{1}H NMR** ($CDCl_3$, 500MHz) of **P10b**

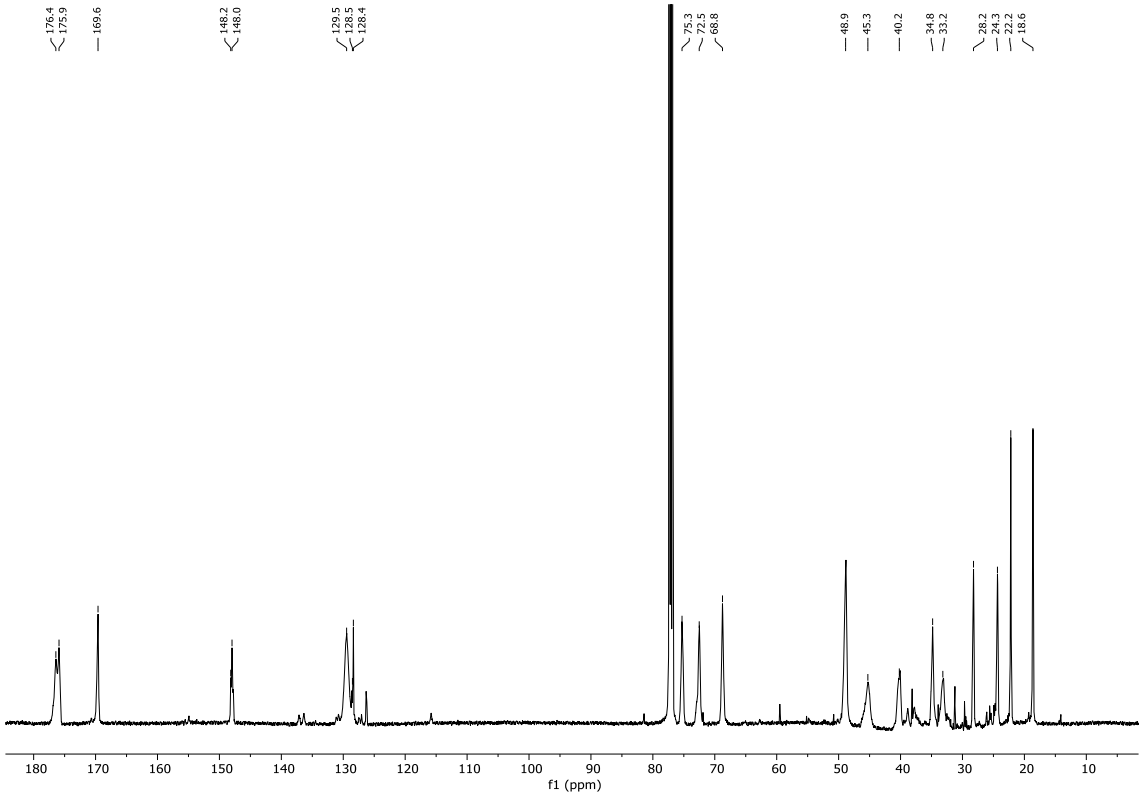


Figure S105: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **P10b**

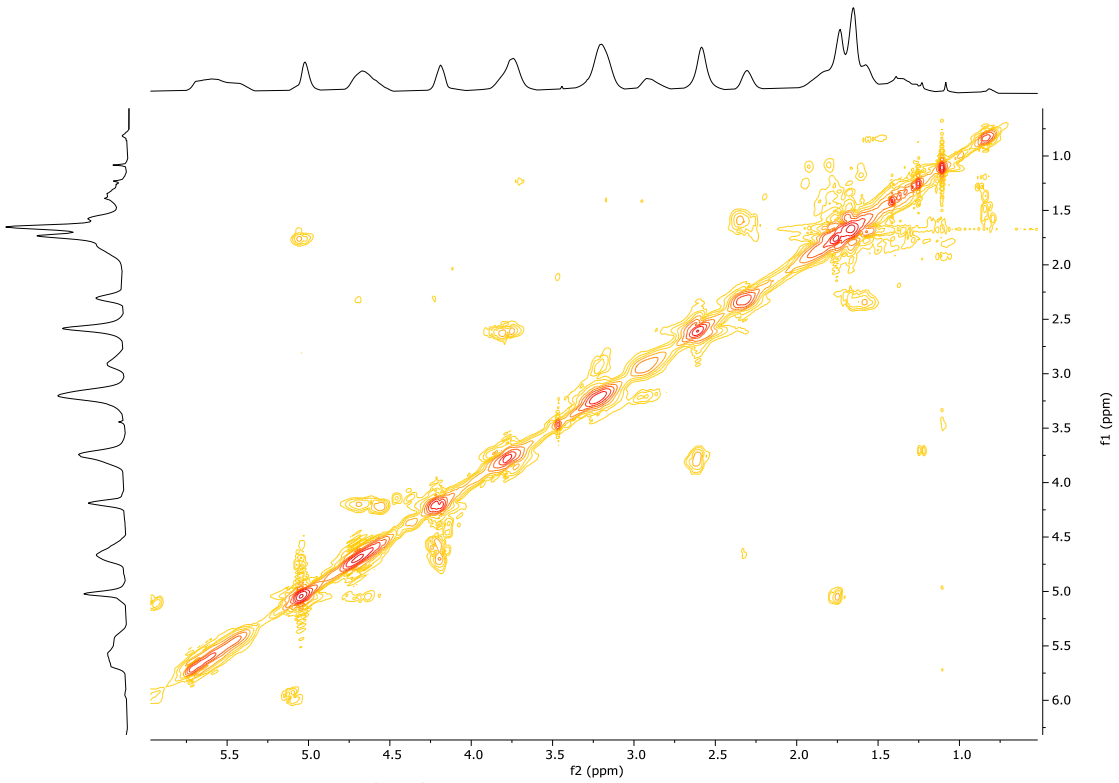


Figure S106: ^{1}**H-**^{1}**H COSY** ($CDCl_3$, 500MHz) of **P10b**

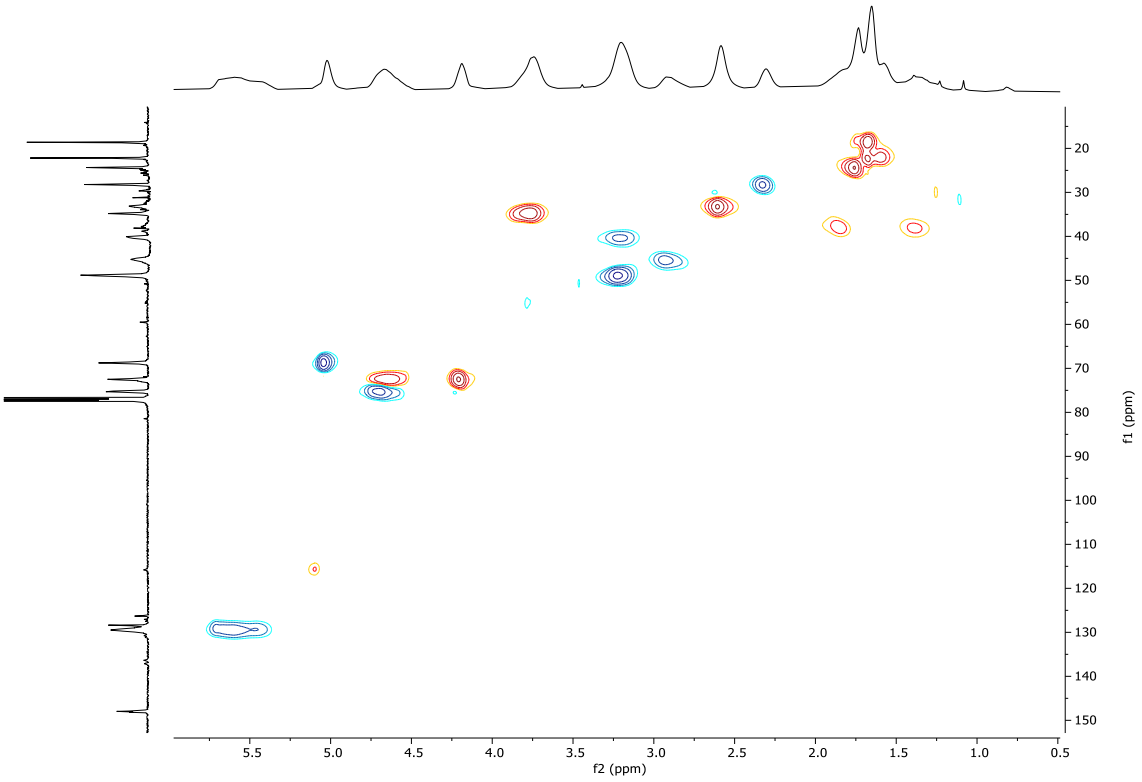


Figure S107: ^{1}**H-**^{13}**C HSQC** ($CDCl_3$, 500MHz) of **P10b**

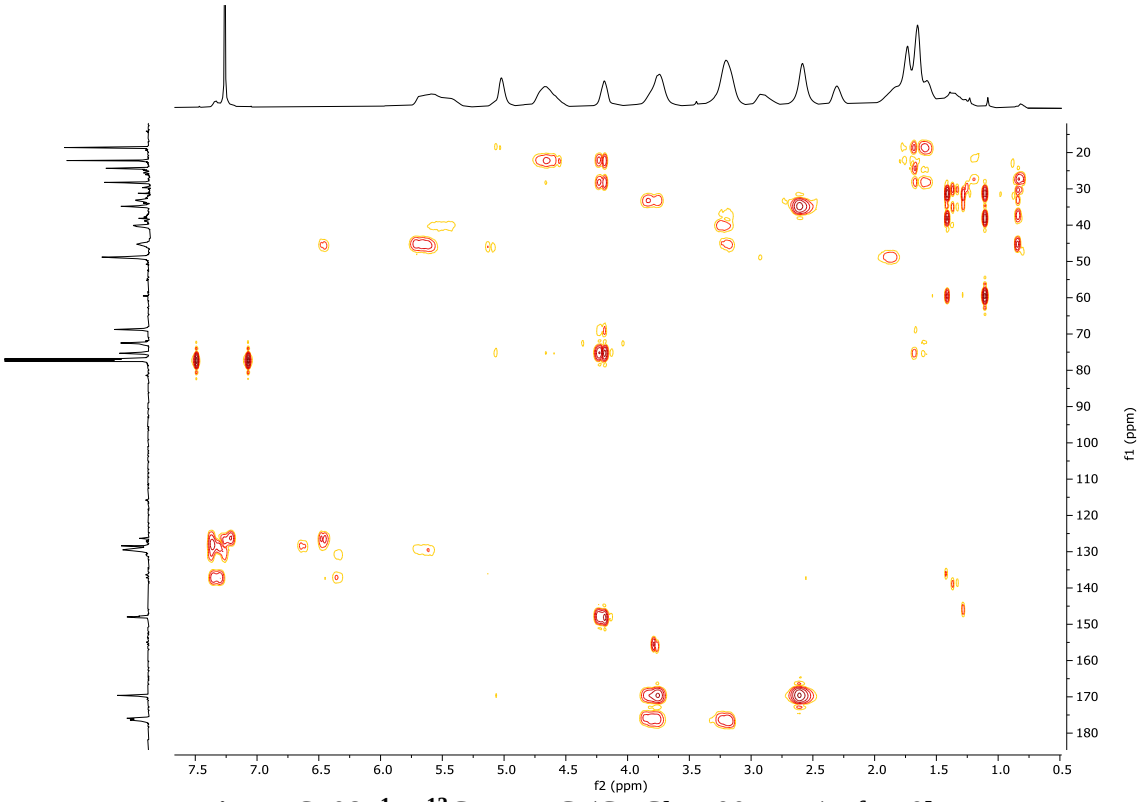


Figure S108: **^{1}H-^{13}C HMBC** ($CDCl_3$, 500 MHz) of **P10b**

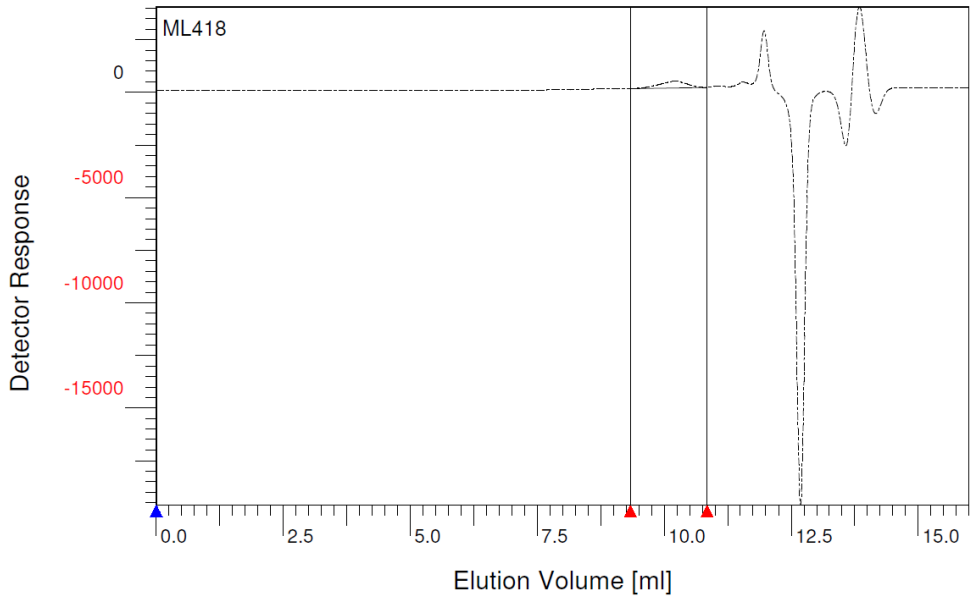


Figure S109: GPC analysis of **P10b**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
4.1273e3	4.5680e3	5.0990e3	4.0318e3	1.1068

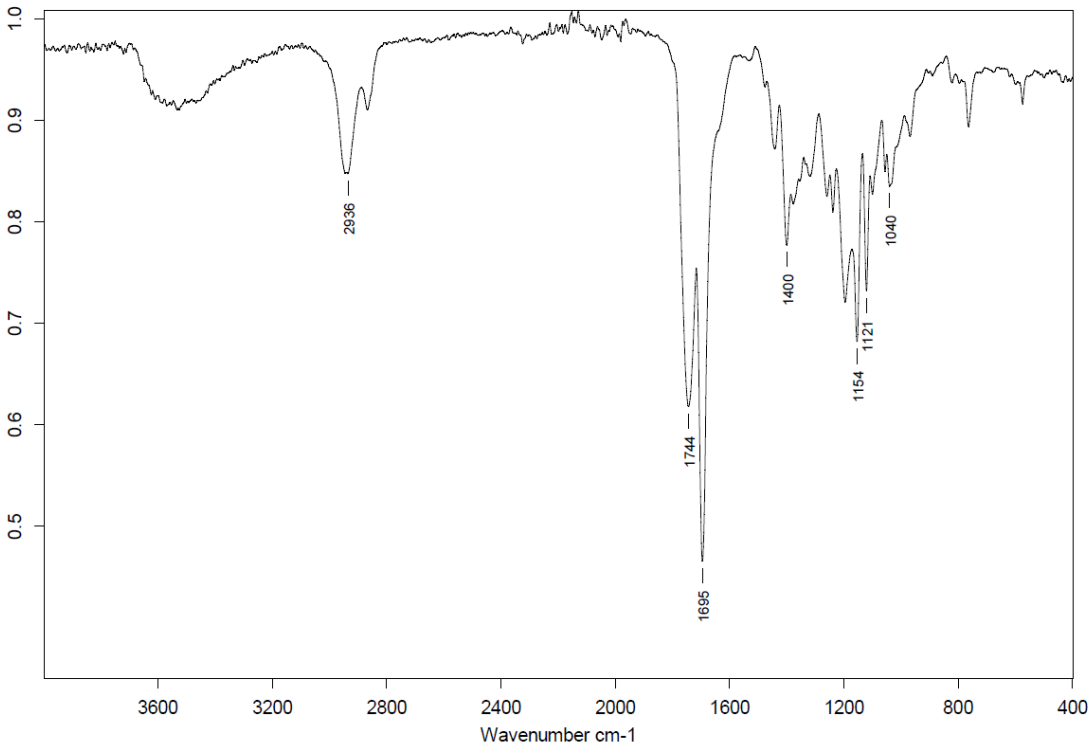


Figure S110: IR spectrum (neat) of **P10b**

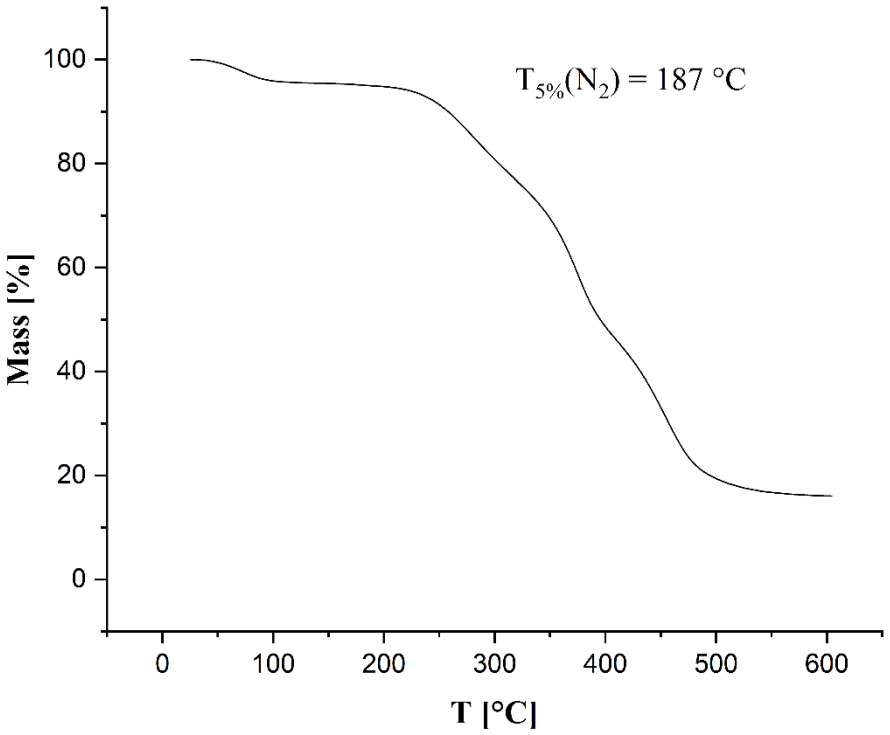


Figure S111: TGA thermogram of **P10b**

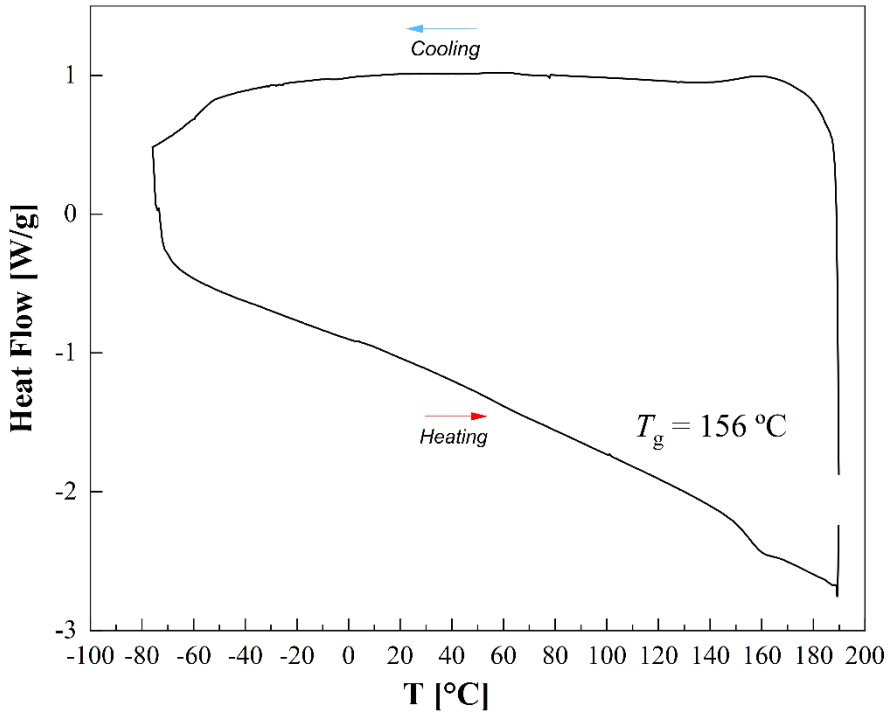


Figure S112: DSC thermogram of **P10b**

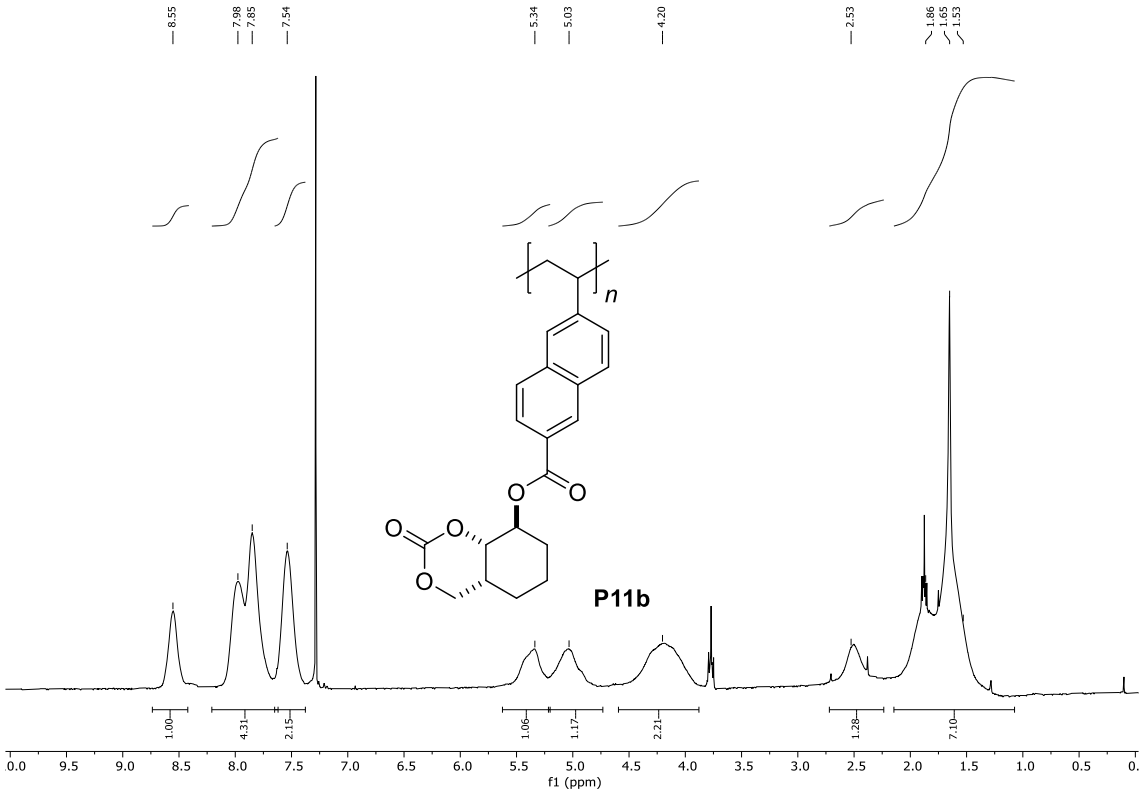


Figure S113: **^{1}H NMR** ($CDCl_3$, 300 MHz) of **P11b**

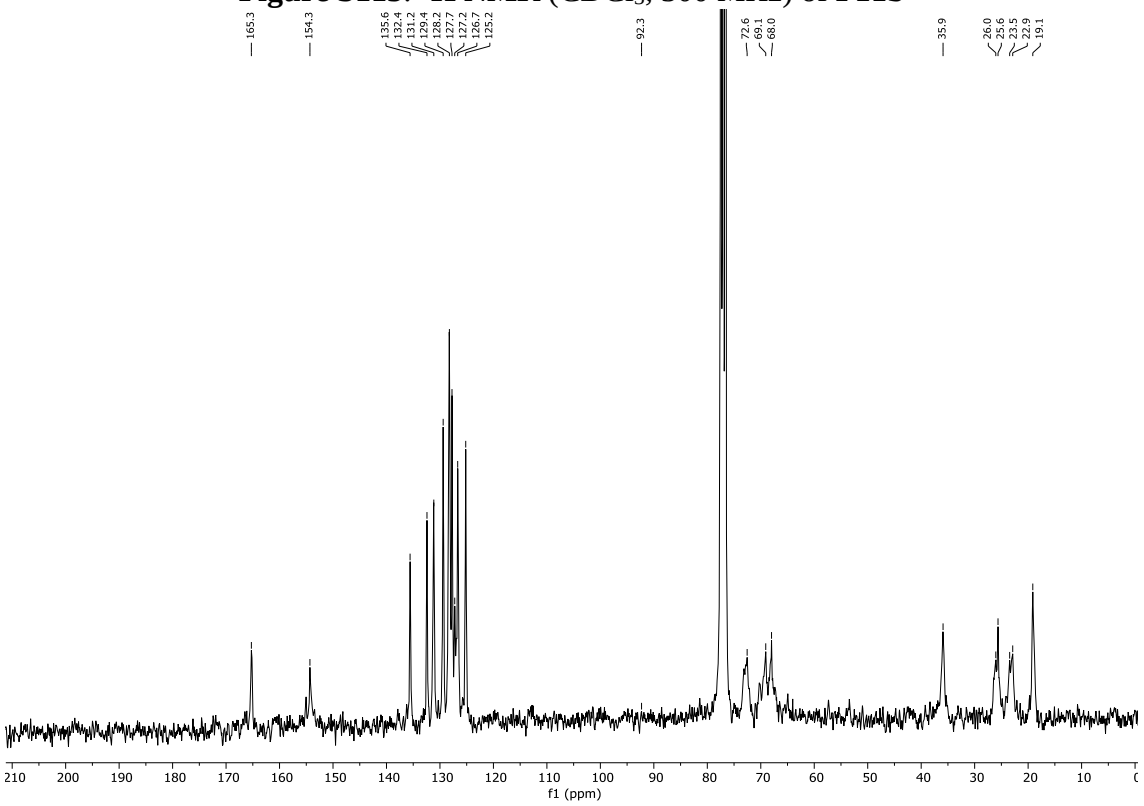


Figure S114: **^{13}C NMR** ($CDCl_3$, 75 MHz) of **P11b**

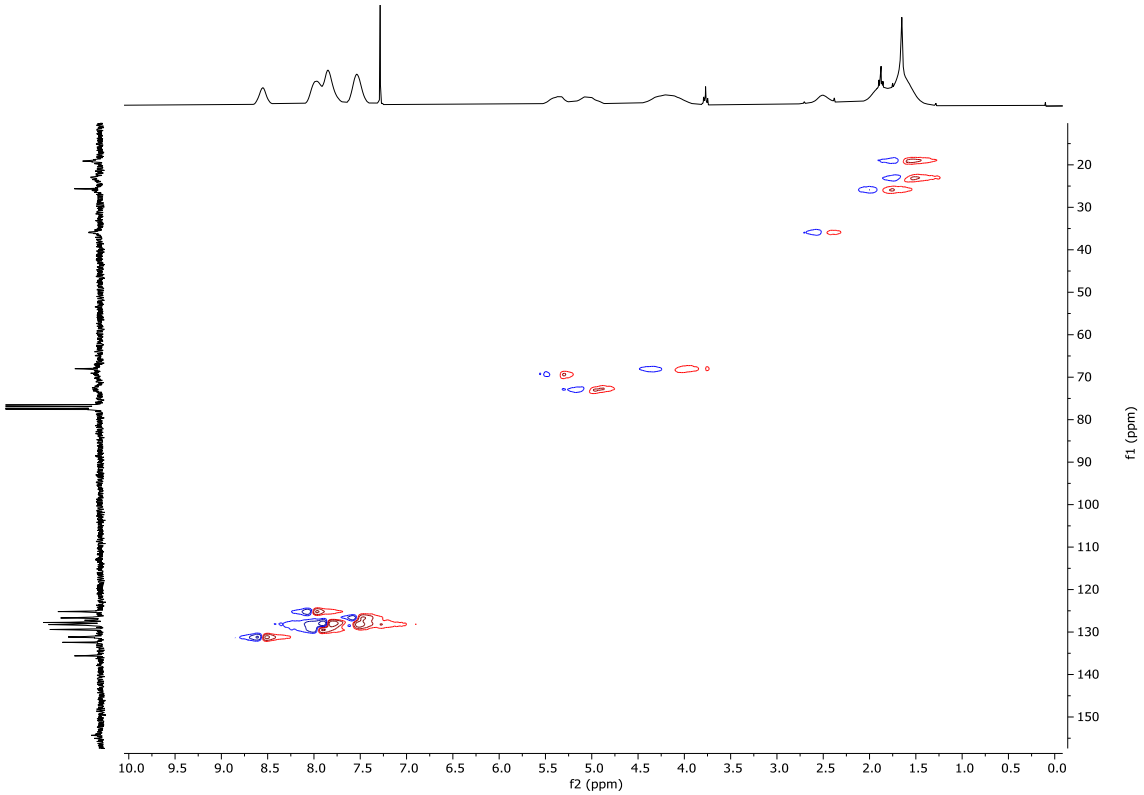


Figure S115: **^{1}H-^{13}C HSQC** ($CDCl_3$, 300 MHz) of **P11b**

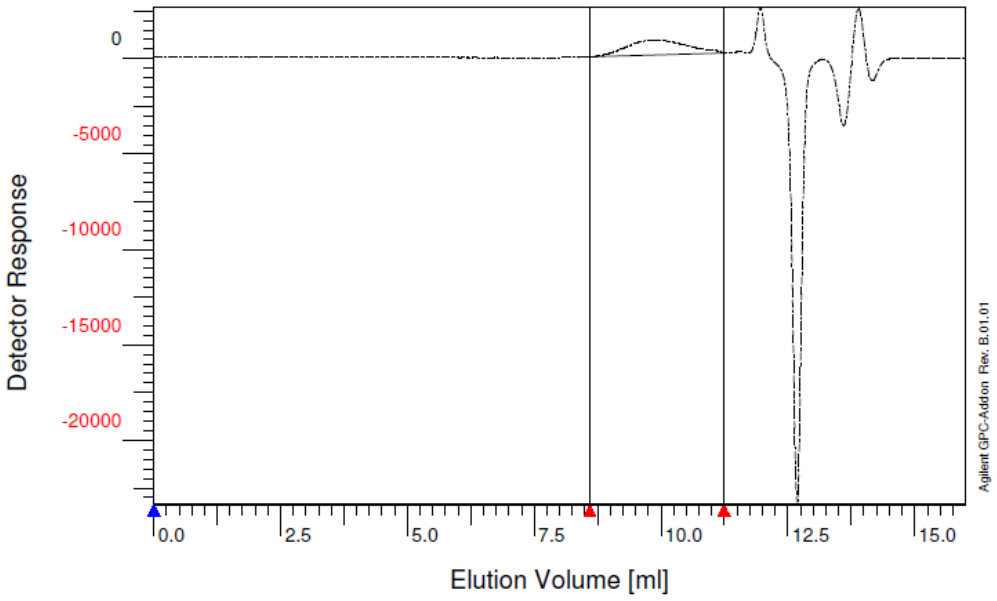


Figure S116: GPC of **P11b**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
4.4735e3	7.0457e3	1.0380e4	6.3393e3	1.5750

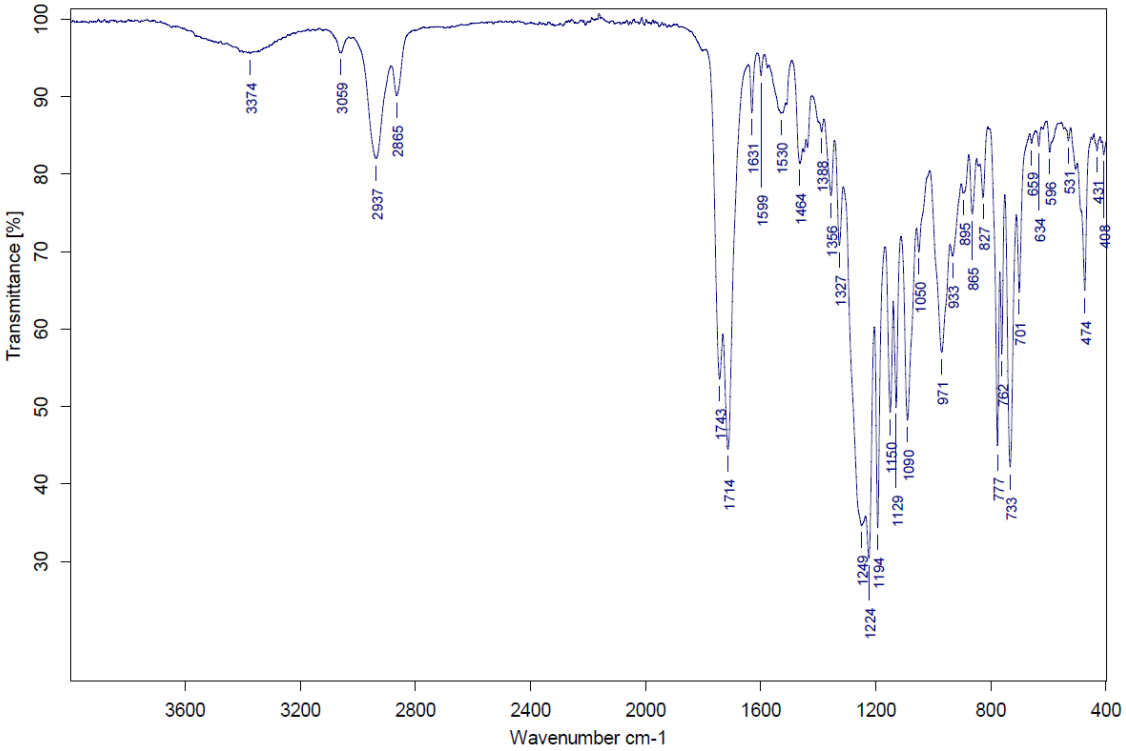


Figure S117: IR spectrum (neat) of **P11b**

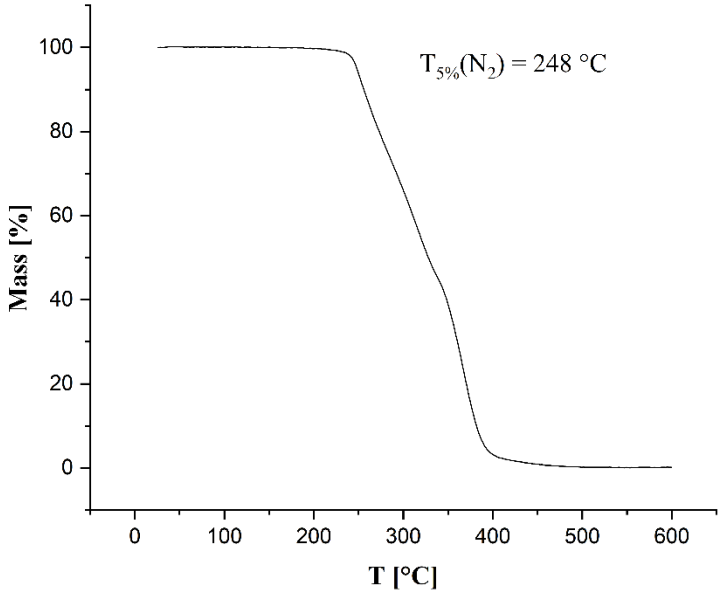


Figure S118: TGA thermogram of **P11b**

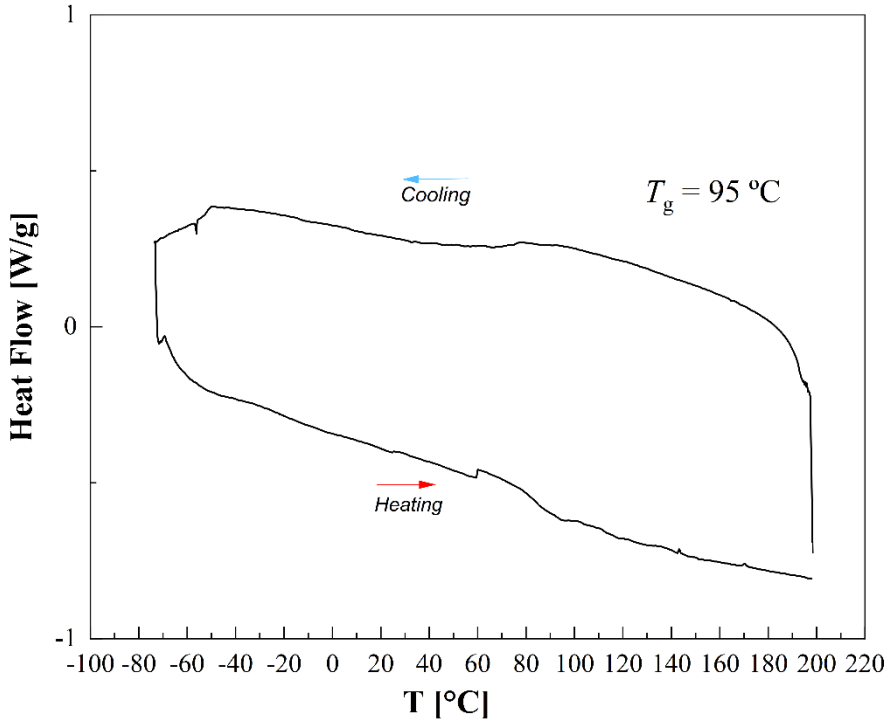


Figure S119: DSC thermogram of **P11b**

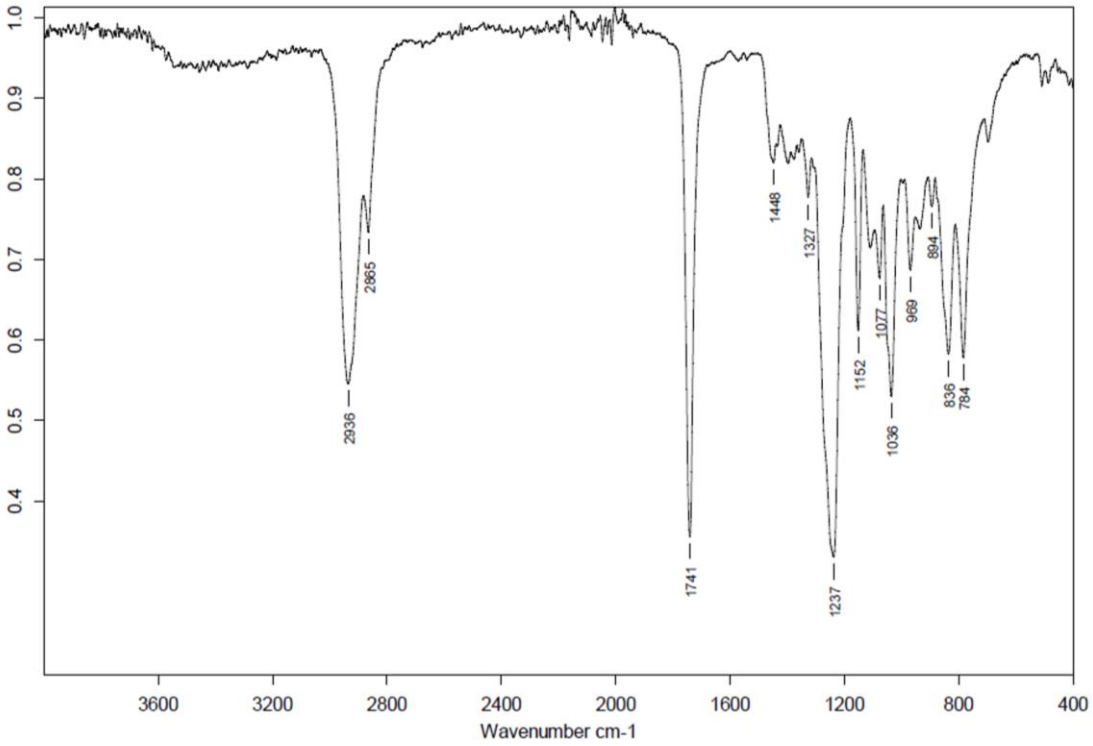


Figure S120: IR spectrum (neat) of **P1a**

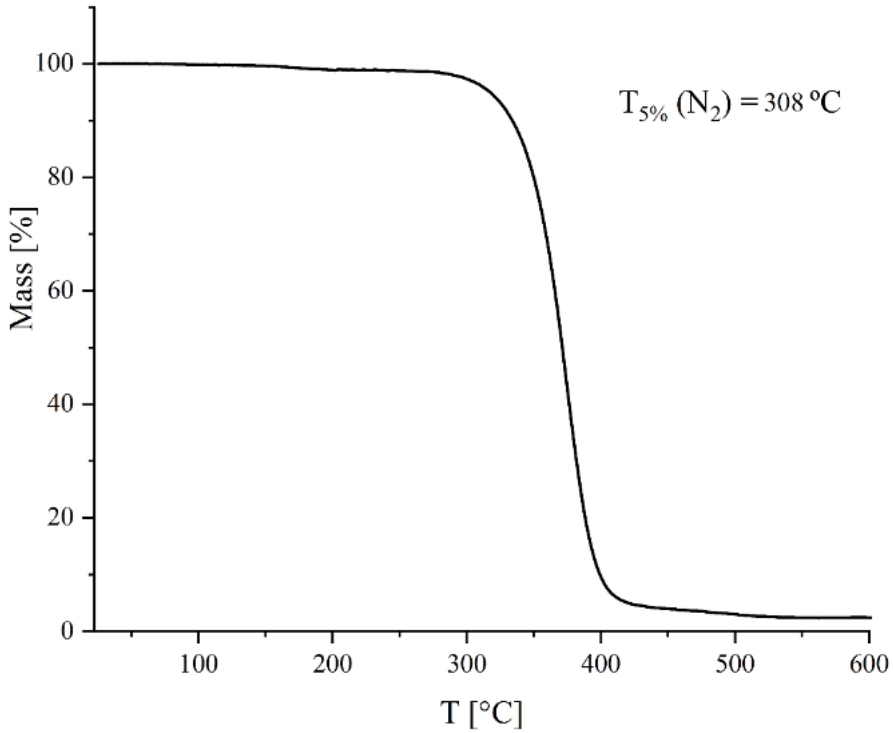


Figure S121: TGA thermogram of **P1a**

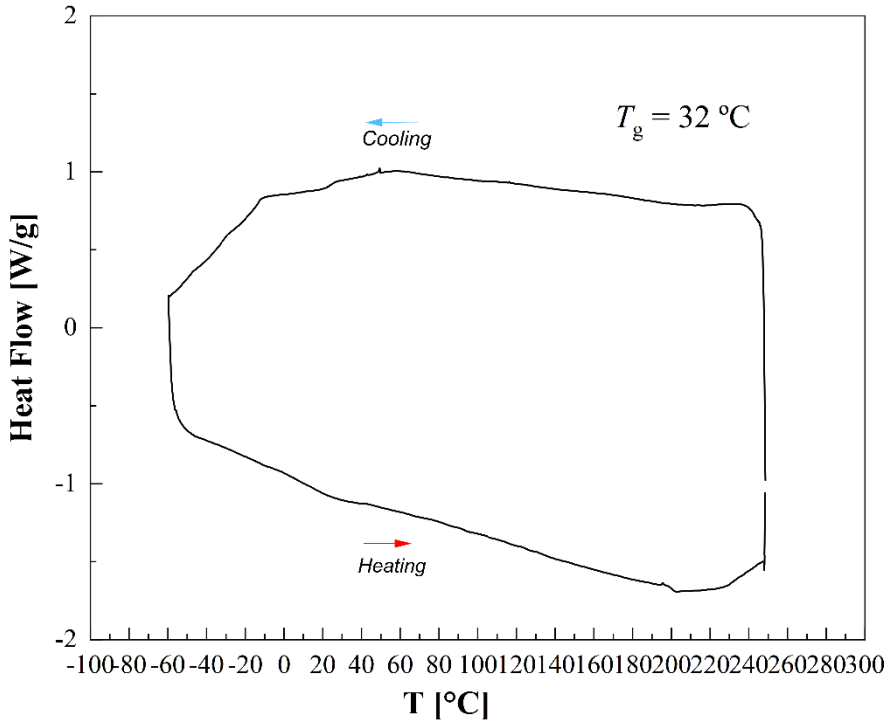


Figure S122: DSC thermogram of **P1a**

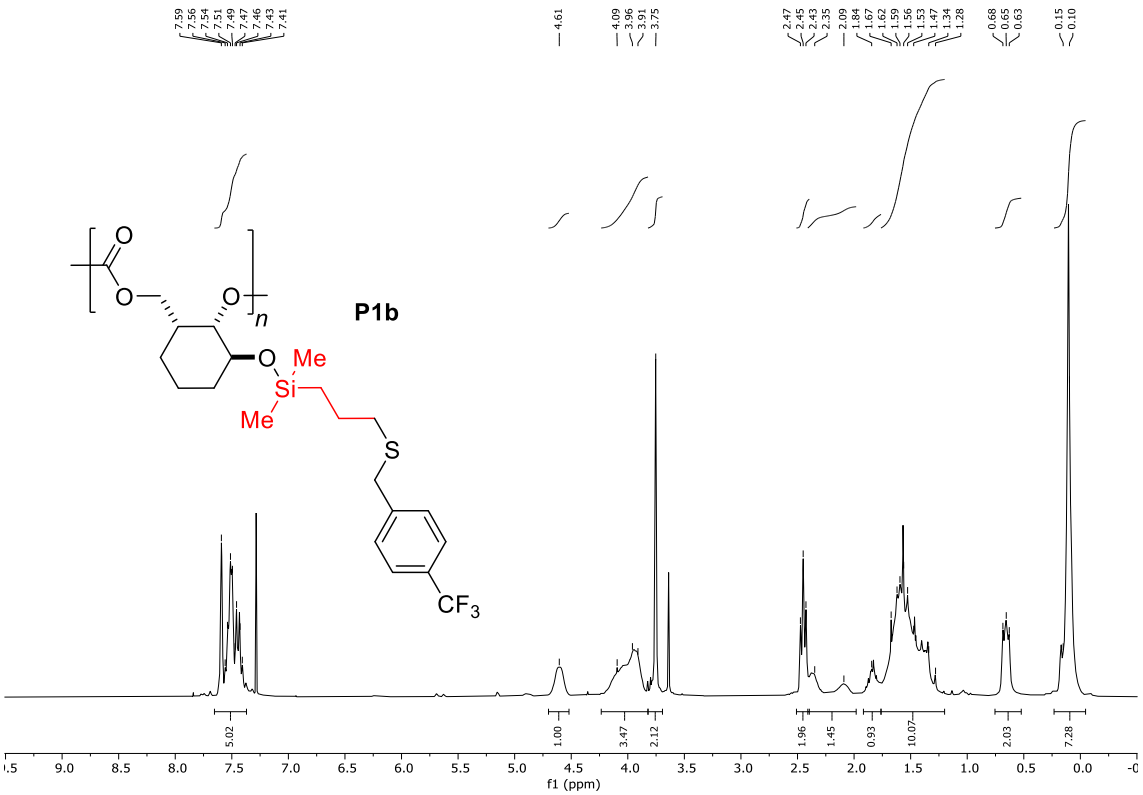


Figure S123: **^{1}H NMR** ($CDCl_3$, 300 MHz) of **P1a**

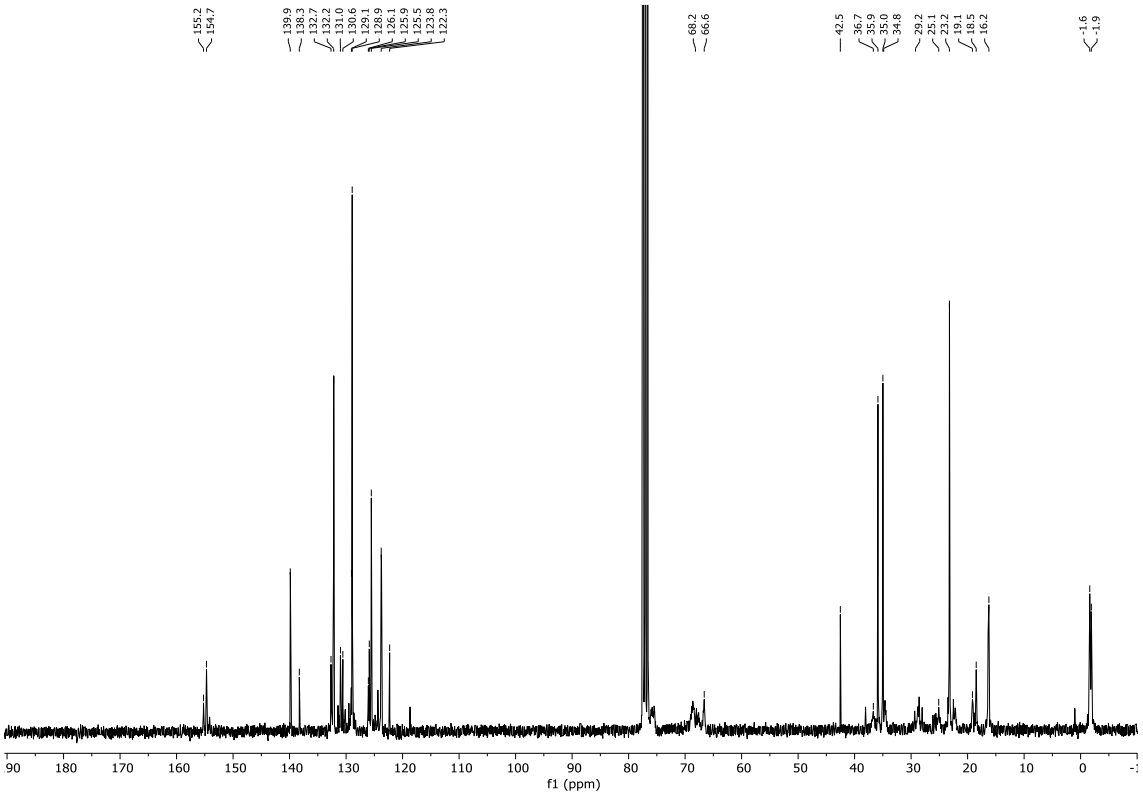


Figure S124: **^{13}C NMR** ($CDCl_3$, 75 MHz) of **P1b**

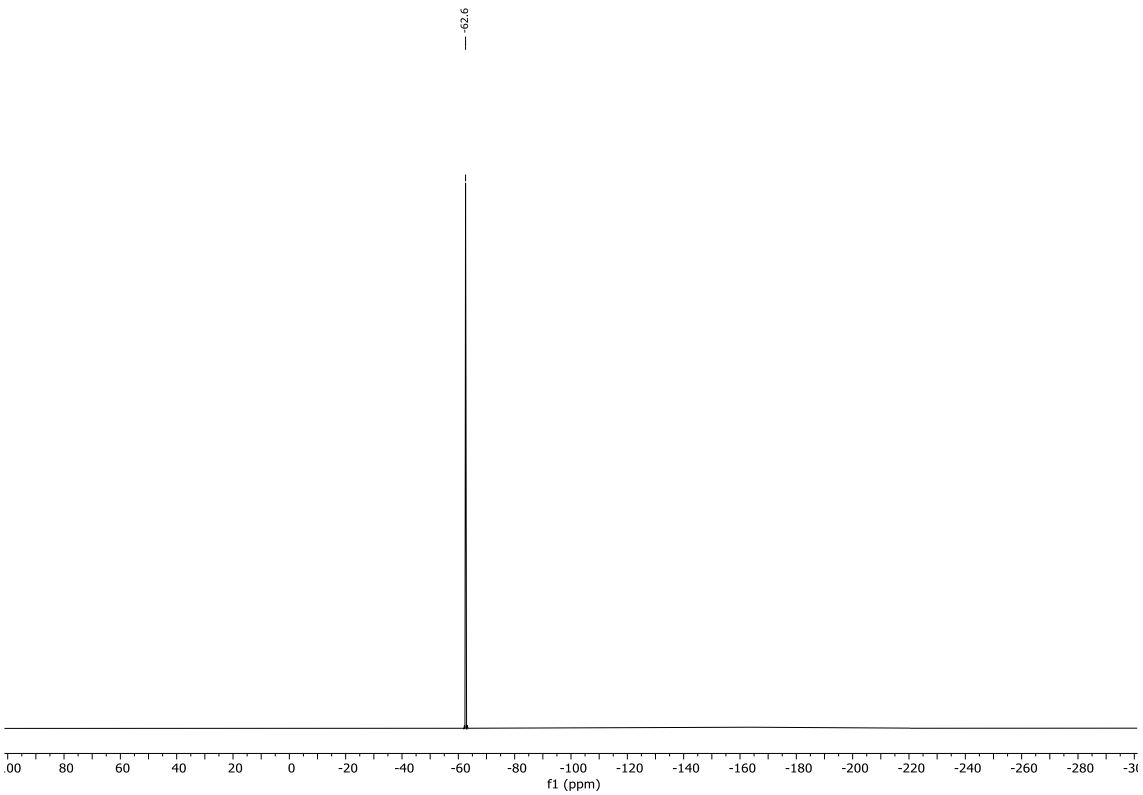


Figure S125: **^{19}F NMR** ($CDCl_3$, 282 MHz) of **P1b**

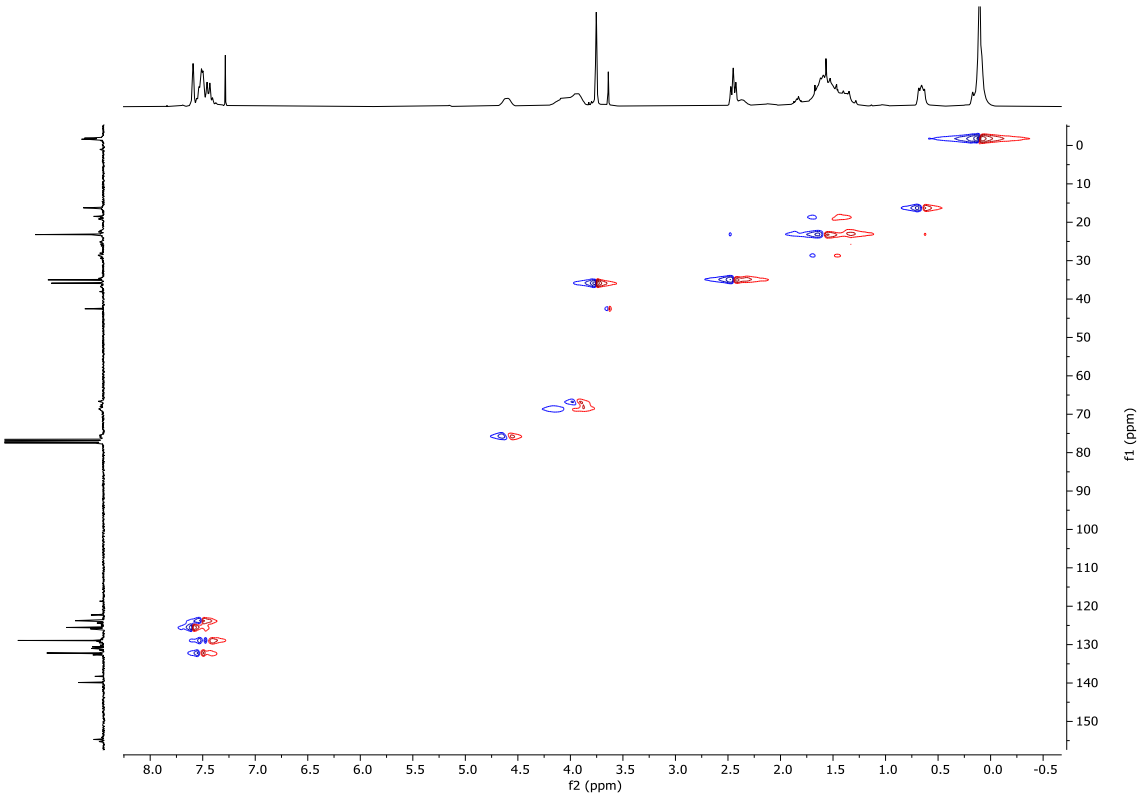


Figure S126: **^{1}H-^{13}C HSQC** ($CDCl_3$, 300 MHz) of **P1b**

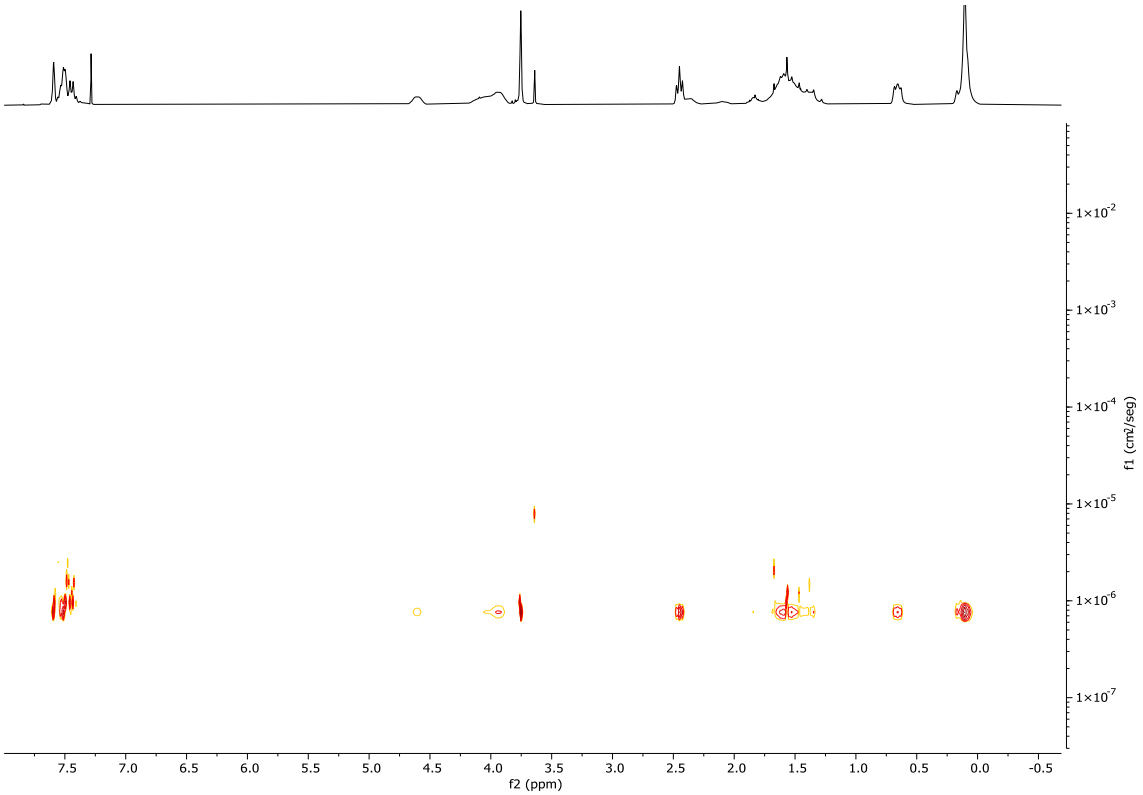


Figure S127: **^{1}H-^{1}H DOSY** ($CDCl_3$, 300 MHz) of **P1b**

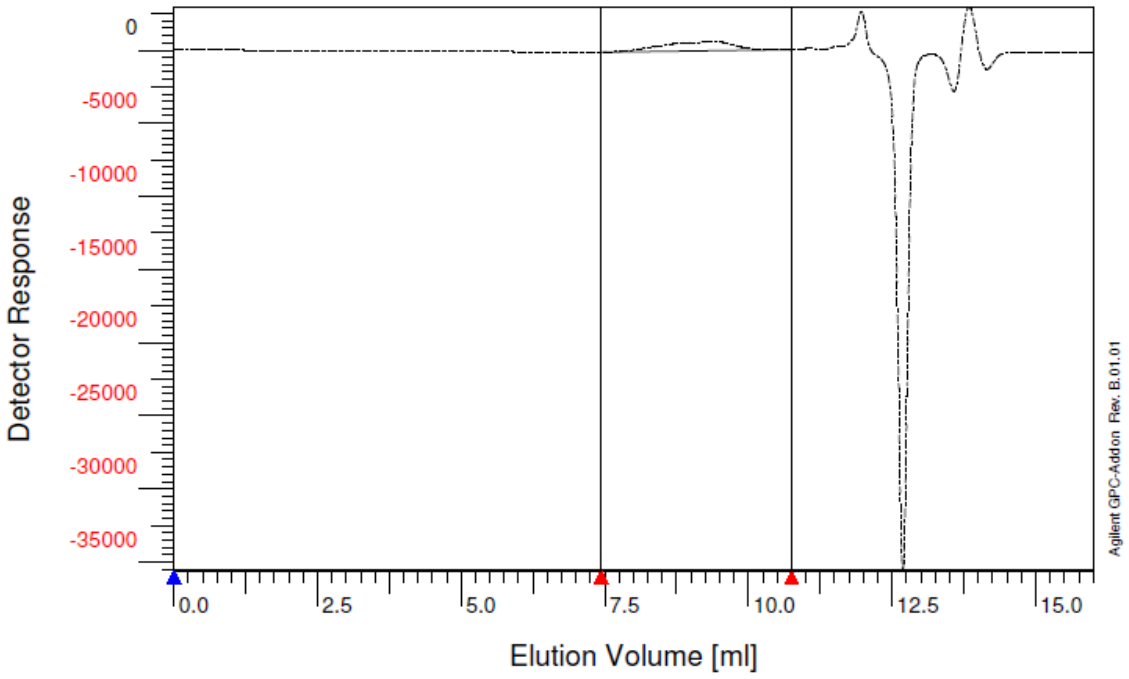


Figure S128: GPC of **P1b**

M_n (g/mol)	M_W (g/mol)	M_z (g/mol)	M_p (g/mol)	Đ
1.2184e4	2.0298e4	4.0261e4	1.1898e4	1.6660

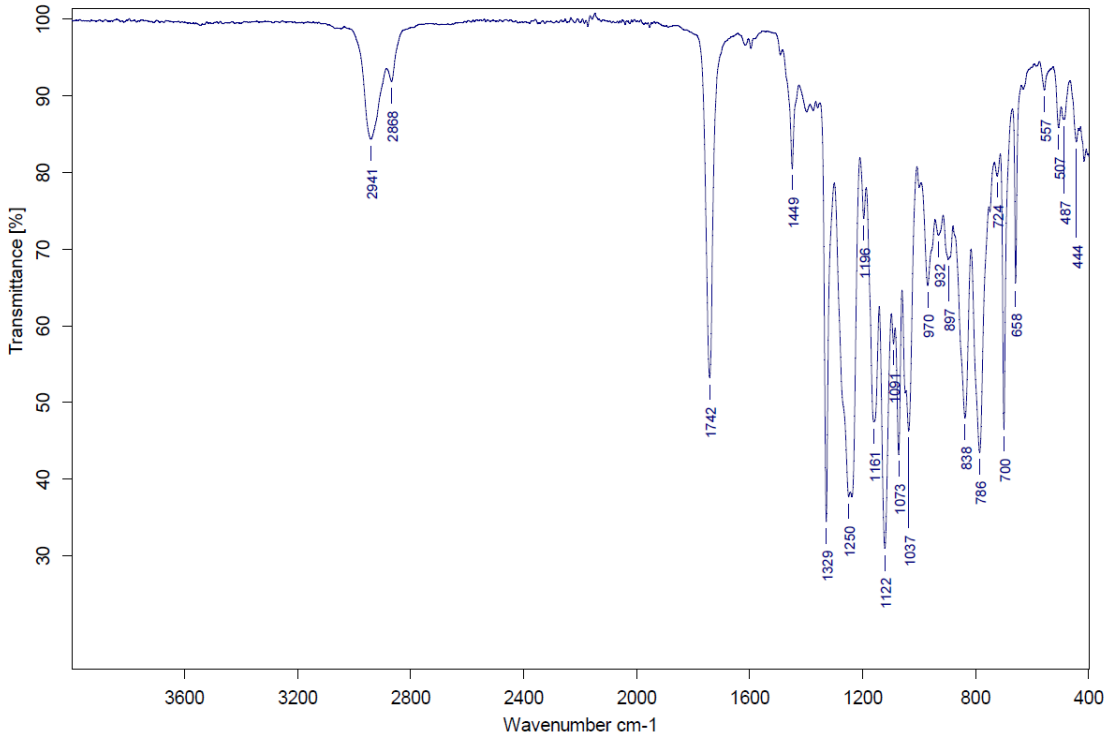


Figure S129: IR spectrum (neat) of **P1Bb**

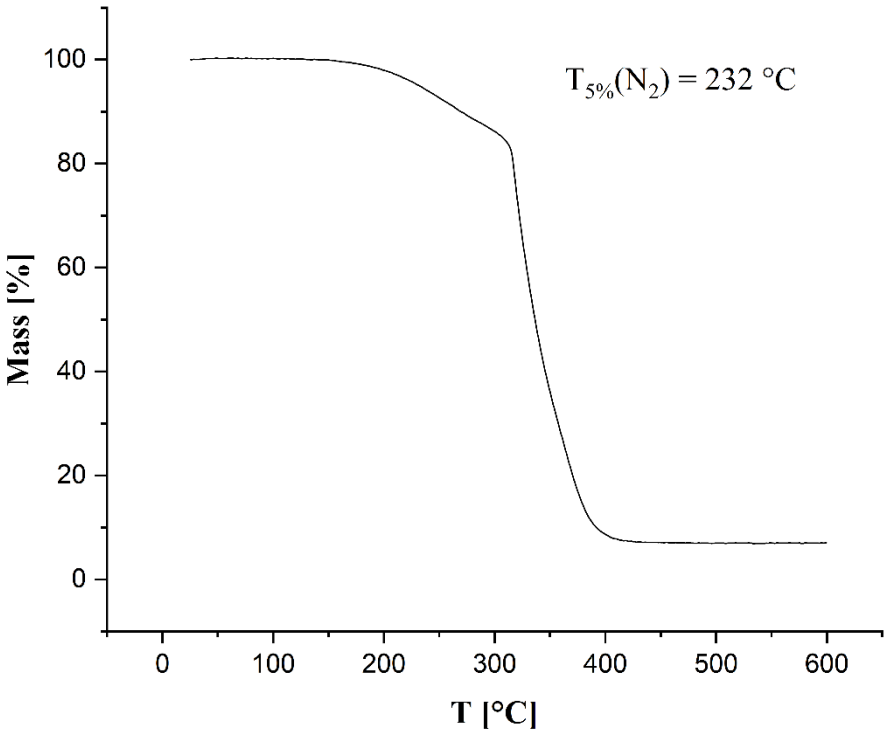


Figure S130: TGA thermogram of **P1b**

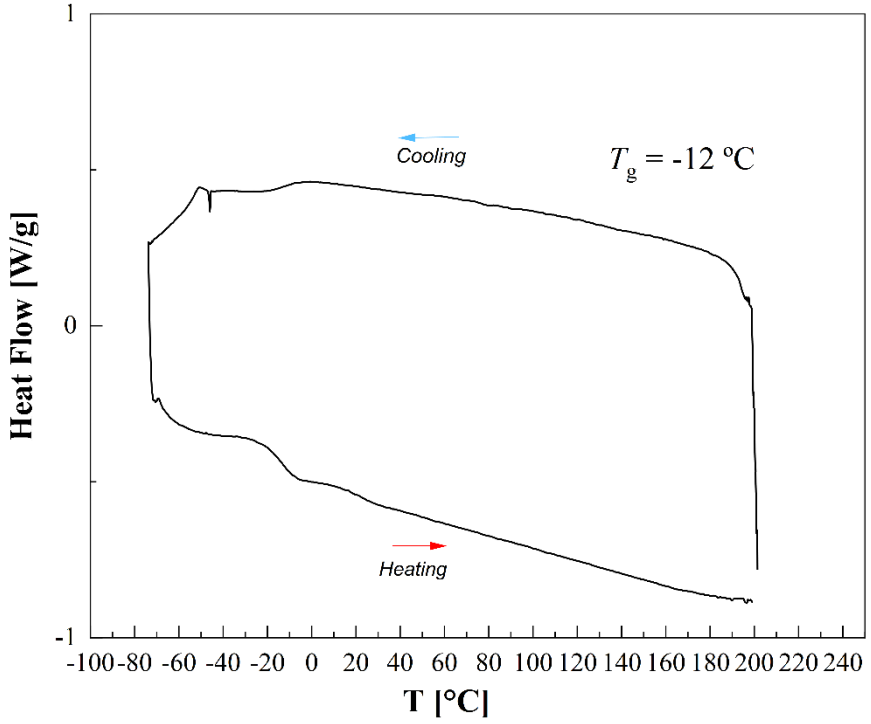


Figure S131: DSC thermogram of **P1b**

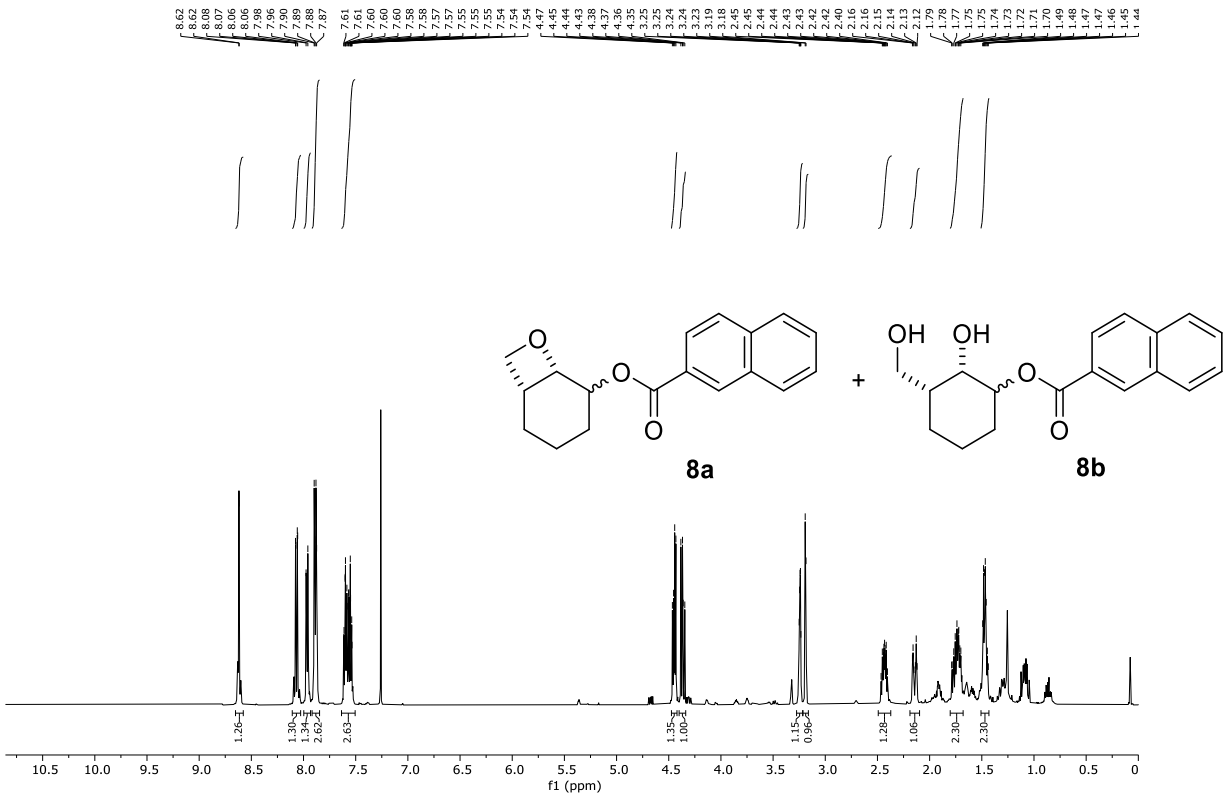


Figure S132: **^{1}H NMR** ($CDCl_3$, 500 MHz) of **8a** and **8b**

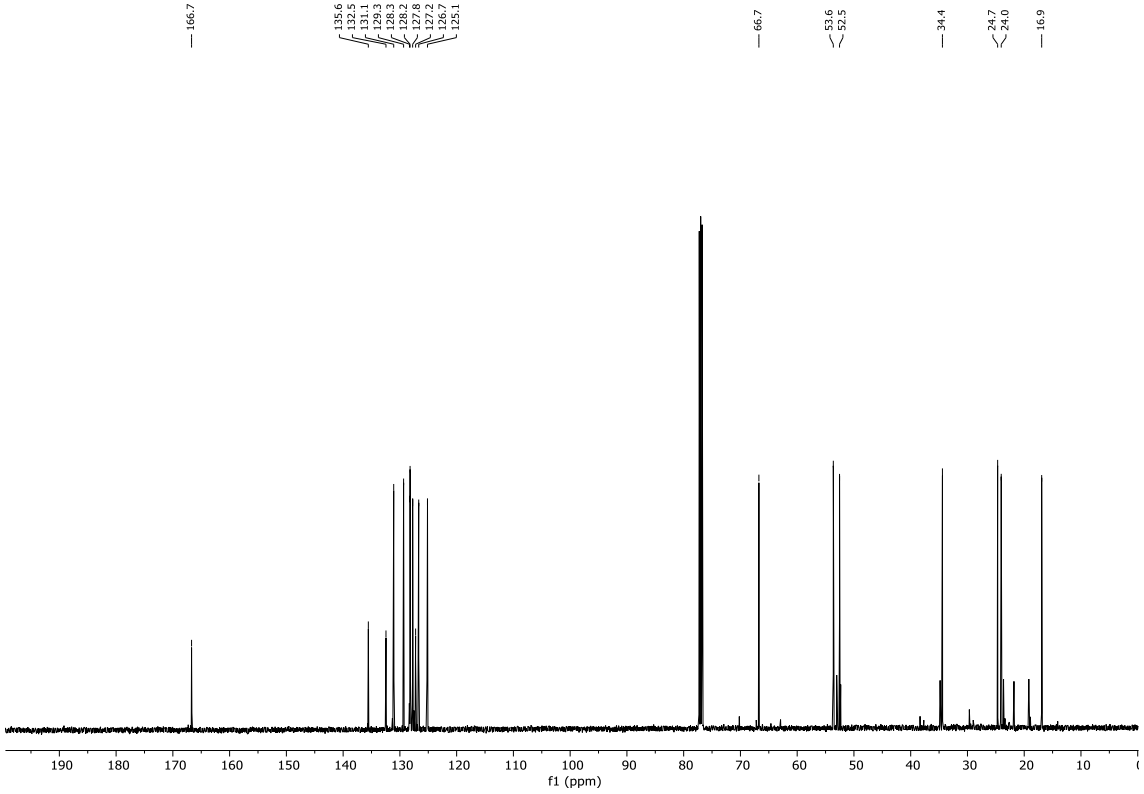
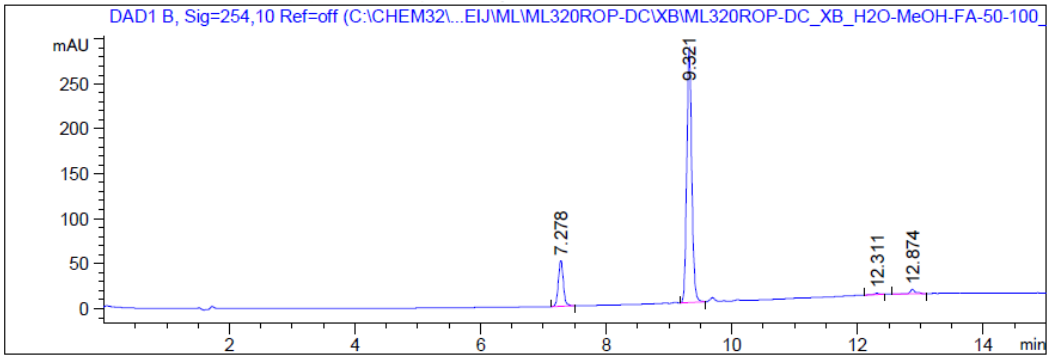


Figure S133: **^{13}C NMR** ($CDCl_3$, 126 MHz) of **8a** and **8b**




```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Do not use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,10 Ref=off

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.278 BB    0.0839  279.29230   50.96851  14.8538
   2   9.321 BB    0.0845 1561.52991  282.45435  83.0482
   3  12.311 BB    0.0738    7.62240    1.59473   0.4054
   4  12.874 BB    0.0939   31.82518    4.89391   1.6926

Totals :                  1880.26979  339.91149
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Figure S134: LCMS of **8a** and **8b**

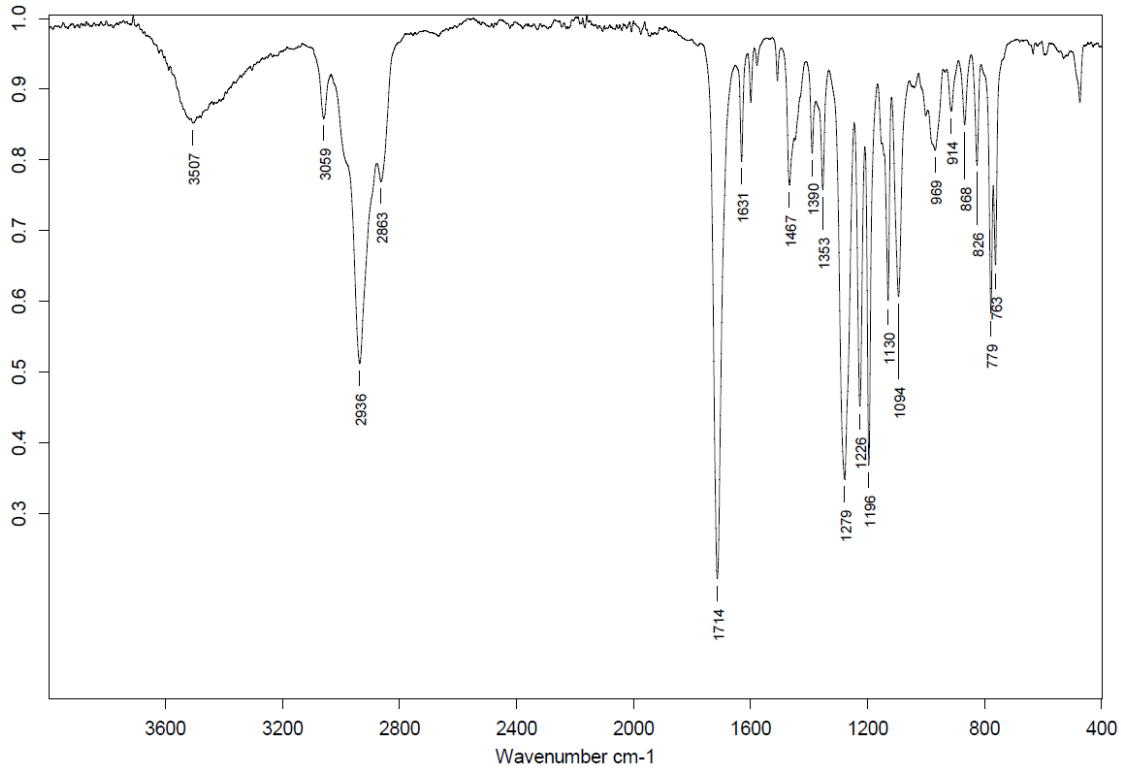

Figure S135: IR spectrum (neat) of **8a** and **8b**